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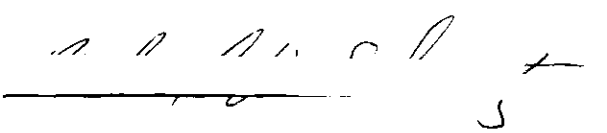

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A STUDY OF SOME REACTIONS OF COMPLEX METAL HYDRIDES WITH MAGNESIUM HALOGEN COMPOUNDS

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SUMMARY

PART I. CONCERNING THE REACTIONS OF LITHIUM, AND SODIUM ALUMINUM HYDRIDE WITH MAGNESIUM HALIDES IN ETHER SOLVENTS

The reaction of complex metal hydrides with magnesium halides in ether solvents can be understood in terms of the two equilibria shown below:

$$MAlH_4 + MgX_2 \rightleftharpoons XMgAlH_4 + MX$$

$$MAlH_4 + XMgAlH_4 \rightleftharpoons Mg(AlH_4)_2 + MX$$

If MX is insoluble, both reactions proceed to the right and $Mg(AlH_4)_2$ is produces. If MX is soluble and $XMgAlH_4$ is insoluble then the first reaction proceeds to the right and the second reaction does not occur. If MX and $XMgAlH_4$ are both soluble, the first reaction lies to the right and the second reaction primarily to the left.

PART II. CONCERNING THE REACTIONS OF LITHIUM, SODIUM AND POTASSIUM HYDRIDES WITH MAGNESIUM HALIDES IN ETHER SOLVENT

The reaction of alkali metal hydrides with magnesium halides in ether solvents provides an excellent method for the preparation of active magnesium hydride in high yield. The reaction of commercial grade lithium hydride with magnesium halides to produce MgH_2 is very slow; however, the reaction using active lithium hydride prepared by hydrogenolysis of t-butyl lithium proceeds at a reasonable rate. Unfortunately generating active lithium hydride by this method is not very convenient. On the

other hand, reaction of commercial grade sodium hydride with magnesium bromide in THF provides a rapid and economic method for preparing active magnesium hydride although by-product NaBr is present as well. If pure magnium hydride is desired, this preparation can be accomplished by reaction of sodium hydride with magnesium iodide in diethyl ether followed by extraction of the by-product NaI with THF. Evidence for compounds of the type Li_nMgH_{2+n} suggested earlier by Wiberg to be formed in the reaction of lithium hydride with magnesium chloride was not found.

Part III. CONCERNING THE EXISTENCE OF $HMgAlH_4$ AND $HMgBH_4$

Seven general methods have been investigated in attempting to prepare $HMgAlH_4$.

$$MH + XMgAlH_4 \longrightarrow MX + HMgAlH_4$$

$$RMgAlH_4 \xrightarrow{\Delta} HMgAlH_4 + \text{Olefin}$$

$$H_2 + RMgAlH_4 \xrightarrow{H_2} RH + HMgAlH_4$$

$$RMgAlH_4 + MH \longrightarrow MR + HMgAlH_4$$

$$Mg(AlH_4)_2 + L \longrightarrow HMgAlH_4 + AlH_3 \cdot L$$

$$MgH_2 + AlH_3 \longrightarrow HMgAlH_4$$

$$MgH_2 + Mg(AlH_4)_2 \longrightarrow 2\ HMgAlH_4$$

In none of these cases was $HMgAlH_4$ or $HMgBH_4$ isolated. Instead a physical mixture of MgH_2 and either $Mg(AlH_4)_2$ or $Mg(BH_4)_2$ was obtained.

In all probability, if $HMgAlH_4$ and $HMgBH_4$ were stable compounds, some of the reactions studied should have produced these compounds. It is concluded, therefore, that $HMgAlH_4$ and $HMgBH_4$ are unstable and, if

formed as intermediates, disproportionate to MgH_2 and $Mg(AlH_4)_2$ or $Mg(BH_4)_2$.

PART IV. CONCERNING THE REACTION OF LITHIUM AND SODIUM ALUMINUM HYDRIDE WITH GRIGNARD REAGENTS IN ETHER SOLVENTS

The reaction of $LiAlH_4$ and $NaAlH_4$ with Grignard reagents has been shown to lead to different products depending on the ratio of the reactants.

$$LiAlH_4 + 6\ n\text{-}C_4H_9MgBr \rightarrow 2\ n\text{-}C_4H_9MgBr + 2\ MgH_2 + MgBr_2 + BrMgAl(n\text{-}C_4H_9)_4$$

$$LiAlH_4 + 4\ n\text{-}C_4H_9MgBr \rightarrow 2\ MgH_2 + MgBr_2 + LiBr + BrMgAl(n\text{-}C_4H_9)_4$$

$$LiAlH_4 + 3\ n\text{-}C_4H_9MgBr \rightarrow MgH_2 + LiBr + 1/2\ MgBr_2 + BrMgAlH(n\text{-}C_4H_9)_3$$

$$LiAlH_4 + 2\ n\text{-}C_4H_9MgBr \rightarrow BrMg_2AlH_4(n\text{-}C_4H_9)_2 + LiBr$$

$$LiAlH_4 + n\text{-}C_4H_9MgBr \rightarrow HMgAlH_3\ n\text{-}C_4H_9 + LiBr$$

Various intermediates involved in the stepwise process, such as $BrMgAlR_4$ and $BrMg_2AlH_4R_2$, have been isolated and characterized. The stability of the $HMgAlH_3R$ compounds produced by the reaction of $LiAlH_4$ with RMgX in 1:1 ratio was found to be dependent on the nature of the alkyl group. When R = $n\text{-}C_4H_9$, C_2H_5 and C_6H_5, the $HMgAlH_3R$ compounds were stable. When R = CH_3 and $s\text{-}C_4H_9$, the compound was found to disproportionate to MgH_2 and $Mg(AlH_3R)_2$. The reaction in THF is very similar to that in diethyl ether except when the alkali metal by-product is insoluble in THF. In this case 10 percent of the magnesium and aluminum were isolated as a physical mixture of MgH_2 and $Mg(AlH_4)_2$ whereas the remainder of the product was found to be $HMgAlH_3R$ in solution.

PART I

CONCERNING THE REACTIONS OF LITHIUM AND SODIUM ALUMINUM HYDRIDE WITH MAGNESIUM HALIDES IN ETHER SOLVENTS

CHAPTER I

INTRODUCTION

The preparation of magnesium aluminum hydride ($Mg(AlH_4)_2$) was first reported in 1950 by Wiberg and Bauer.[1-3] The preparation of this new hydride was reported by two different synthetic routes represented by Eqs. 1-2.

$$4\ MgH_2 + 2\ AlCl_3 \rightarrow Mg(AlH_4)_2 + 3\ MgCl_2 \quad (1)$$

$$2\ LiAlH_4 + MgBr_2 \rightarrow Mg(AlH_4)_2 + 2\ LiBr \quad (2)$$

Magnesium hydride (MgH_2) was reported to react with aluminum chloride ($AlCl_3$)[1-3] in diethyl ether to produce $Mg(AlH_4)_2$ whereas the second method involved the reaction of $LiAlH_4$ with $MgBr_2$ in diethyl ether.[1,2] The $Mg(AlH_4)_2$ produced was reported to be soluble in diethyl ether and to decompose at 140°, however few experimental details concerning the preparations were given.

Hertwig[4] reported the preparation of $Mg(AlH_4)_2$ by hydrogenolysis of a Grignard reagent in diethyl ether followed by the addition of aluminum chloride to the reaction product. The following series of reactions were suggested to describe the course of the reaction.

$$4\ RMgX + AlX_3 + 4\ H_2 \dashrightarrow XMgAlH_4 + 3\ MgX_2 + 4\ RH \quad (3)$$

$$3\ RMgX + AlX_3 + 3\ H_2 \dashrightarrow AlH_3 + 3\ MgX_2 + 3\ RH \quad (4)$$

$$2\ XMgAlH_4 \longrightarrow Mg(AlH_4)_2 + MgX_2 \quad (5)$$

However again few experimental details were given. Hertwig's[4] report seemed reasonable since it has been shown that hydrogenolysis[5] of Grignard reagents produces a mixture of MgH_2 and magnesium halide. Therefore, the MgH_2 produced by hydrogenolysis of the Grignard compound in the reaction reported by Hertwig could have reacted with $AlCl_3$ to form $Mg(AlH_4)_2$ in a way similar to that previously reported by Wiberg. The suggested $XMgAlH_4$ could then have arisen from the redistribution of $Mg(AlH_4)_2$ and $MgCl_2$.

Earlier Ashby and co-workers prepared $Mg(AlH_4)_2$ by the reaction of $NaAlH_4$ and $MgCl_2$ in dimethyl ether[6] and noticed that the physical properties of this compound were different from the properties reported by Wiberg for $Mg(AlH_4)_2$. The $Mg(AlH_4)_2$ prepared by Ashby was insoluble in diethyl ether and decomposed at 180°C.

In 1966 Czech workers[7] verified the preparation of $Mg(AlH_4)_2$ by the reaction of $NaAlH_4$ and $MgCl_2$. Although elemental analysis data were presented, no infrared or X-ray powder diffraction data was given.

It would appear that there is some confusion in the literature concerning the preparation and properties of $Mg(AlH_4)_2$. Since the reaction of a complex metal hydride with MgX_2 in ether solvent to produce $Mg(AlH_4)_2$ is such a fundamental reaction, it was decided to study this reaction in detail.

CHAPTER II

EXPERIMENTAL SECTION

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and water[8] or on the bench using typical Schlenk tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

Instrumentation

Infrared spectra were obtained using a Perkin Elmer model 621 High Resolution Infrared Spectrophotometer. Sodium chloride cells were used. Spectra of solids were obtained in nujol which had been dried over sodium wire and stored in a dry box. No change was observed in the spectra of either solutions or mulls after standing in the cell for some time. It is therefore concluded that there is no interaction of the products studied with the cell windows.

X-ray powder diffraction patterns were run using a Debye-Scherrer camera of 114.6 mm diameter using CuK_{α}(1.540A°) radiation with a nickel filter. Single walled capillaries of 0.5 mm diameter were used. These were filled in the dry box and sealed with a microburner.

Reagents

Tetrahydrofuran and benzene (Fisher Certified reagent) were distilled over sodium aluminum hydride immediately before use. Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum

hydride immediately prior to use.

Mercuric halides (Baker Analyzed) were dried under vacuum and used without further purification. Triply sublimed magnesium was obtained from Dow Chemical Company. It was washed with diethyl ether and dried under vacuum prior to use.

Lithium and sodium aluminum hydride were obtained from Ventron Metal Hydrides Division. Diethyl ether and tetrahydrofuran solutions of these complex metal hydrides were prepared by adding dry freshly distilled solvent to an appropriate amount of the solid complex metal hydride. The resulting solution was then filtered through a coarse glass fritted filter funnel to which had been added dried Celite filter aid. The resulting clear solutions were standardized by EDTA titration of aluminum.

Analytical Procedures

Halogen analysis was carried out by the Volhard method. Aluminum analysis was carried out by titration with EDTA. Magnesium analysis in the presence of aluminum was carried out by masking the aluminum with triethanol amine. Lithium analysis was carried out by flame photometry. Hydridic hydrogen analysis was carried out by hydrolyzing a weighed sample of the compound and measuring the volume of gas evolved after passing it through a liquid nitrogen trap to remove ether. The amount of ether solvated to a compound was assumed by difference.

Preparations and Procedures

General Procedures for Infrared Studies

A measured amount of magnesium halide in solution was added to a 3 neck 500 ml round bottom flask equipped with a 3 way stopcock, an addition funnel, and a dry ice condenser. The solution of alkali metal aluminum hydride was added in a stepwise fashion in order to establish $MAlH_4$:MgX_2 mole ratios of 0.5:1.0; 1.0:1.0; 1.5:1.0; 2.0:1.0; 3.0:1.0. After each addition the solution was stirred for fifteen minutes and any precipitate formed was allowed to settle. A sample of the supernatant liquid was taken with a syringe through the three way stopcock (under strong nitrogen flush) and the infrared cell filled in the dry box. All reactions were carried out such that the resulting concentration of the reaction mixture was between 0.1 and 0.2M.

General Procedure for the Isolation of Intermediates

The alkali metal aluminum hydride was added to the magnesium halide in a ratio of 1.0:1.0. Any solid formed at this ratio was filtered, analyzed, and its infrared spectrum and X-ray powder pattern obtained. The resulting solutions were then fractionally crystallized and the separate fractions analyzed, and the infrared spectrum and X-ray powder pattern of each obtained.

Preparation of Magnesium Halides in Diethyl Ether and Tetrahydrofuran[9,10]

In a typical preparation of magnesium halides in ether solvents, 2 gm of magnesium were added to 20 gm of the appropriate mercuric halide in a 500 ml found bottom flask with a magnetic stirring bar. Two hundred and fifty milliliters of diethyl ether were then distilled into the

flask containing the mixture. The solution was stirred overnight and filtered. The solutions were then standardized by magnesium analysis (EDTA) and halogen analysis (Volhard method). The magnesium to halogen ratio was 1.0:2.00± 0.05 in all cases. A qualitative test for residual mercury in the solutions was negative using ferrocyanide and 2,2'-dipyridyl. The solutions were also tested for solvent impurities by hydrolyzing a sample of the solution with distilled water in benzene. The organic matter was then salted out of the water layer into the benzene. The benzene layer was then subjected to analysis by glc. Only diethyl ether was found to be present in the original solution of MgX_2.

A different method for the preparation of magnesium chloride in diethyl ether had to be used. This was necessary since $MgCl_2$ is insoluble in diethyl ether and it would have been difficult to separate the $MgCl_2$ from the Hg by-product in the previous method. Anhydrous hydrogen chloride in diethyl ether was added to a diethyl ether solution of ethyl magnesium chloride at room temperature in 1:1 molar ratio. The precipitate which was formed was washed with diethyl ether and dried under vacuum. Anal. Calcd. for $MgCl_2 \cdot (C_2H_5)_2O$:Mg, 14.36; Cl, 41.89. Found: Mg, 14.30; Cl, 41.29.

A. Reactions of $NaAlH_4$ and MgX_2 in Tetrahydrofuran

(1) Reaction of Sodium Aluminum Hydride and Magnesium Chloride in Tetrahydrofuran. When $NaAlH_4$ was added to $MgCl_2$ in THF in a mole ratio of 0.5:1.0 a precipitate was formed. The infrared spectrum of the solution at this point showed bands at 1715, 795, and 760 cm^{-1}. At a $NaAlH_4$:$MgCl_2$ ratio of 1.0:1.0 the bands at 1715 and 795 cm^{-1} increased

in intensity and more precipitate was formed. Elemental analysis and an X-ray powder pattern of this solid showed it to be NaCl. At a $NaAlH_4$:$MgCl_2$ ratio of 1.5:1, the intensity of the infrared bands noted above decreased and more precipitate was formed. At 2.0:1.0 ratio, no infrared bands appeared in the Al-H stretching and deformation regions and more precipitate formed. At a 3.0:1.0 ratio bands appeared at 1680 and 772 cm^{-1} characteristic of $NaAlH_4$ in tetrahydrofuran. No more precipitate was formed. The solid was filtered and gave an X-ray powder pattern consisting of lines for NaCl and some other substance. This solid was then subjected to soxhlet extration with tetrahydrofuran. A white solid was obtained from this extraction which gave lines in the powder pattern which were the same as the lines in the previous pattern with the NaCl lines subtracted. (See Table III). The infrared spectrum of this solid showed absorption bands at 1725, 1025, 920, 875, 785, and 740 cm^{-1}. A yield of 77% of $Mg(AlH_4)_2 \cdot 4THF$ was obtained. Anal. Calcd. for $Mg(AlH_4)_2 \cdot 4THF$: Mg, 6.49; Al, 14.41; H, 2.13. Found: Mg, 7.06; Al, 14.90; H, 2.24.

In a separate experiment, $NaAlH_4$ was added to $MgCl_2$ in tetrahydrofuran in a mole ratio of 1.0:1.0. A precipitate formed which was filtered. The resulting filtrate was then subjected to crystallization by solvent removal. The infrared spectrum of this solid in nujol gave bands at 1730, 1070, 1030, 920, 880 and 745 cm^{-1}. For the major lines in the X-ray powder pattern see Table III. Anal. Calcd. for $ClMgAlH_4 \cdot 4THF$: Cl, 9.36; Mg, 6.41; Al, 7.12; H, 1.05. Found: Cl, 9.58; Mg, 6.77; Al, 7.22; H, 1.13.

(2) Sodium Aluminum Hydride and Magnesium Bromide in Tetrahydrofuran. The course of the reaction of $NaAlH_4$ and $MgBr_2$ in tetrahydrofuran was followed by infrared analysis. The results were similar to those reported for the previous system.

In a separate experiment, the solution containing the reaction product of $NaAlH_4$ and $MgBr_2$ in a mole ratio of 1.0:1.0 was treated in the same way as the $ClMgAlH_4$ solution. The infrared spectrum of the solid in nujol gave absorption bands at 1715, 1070, 1030, 915, 875, 795, and 745 cm^{-1}. The X-ray powder pattern is shown in Table II. Anal. Calcd. for $BrMgAlH_4 \cdot 4THF$: Br, 18.88; Mg, 5.74; Al, 6.37; H, 0.94. Found: Br, 19.49; Mg, 6.40; Al, 6.91; H, 0.96.

(3) Sodium Aluminum Hydride and Magnesium Iodide in Tetrahydrofuran. At 0.5:1.0 addition of a solution of $NaAlH_4$ in tetrahydrofuran to solid MgI_2 in tetrahydrofuran, the infrared analysis of the filtrate showed an absorption band at 1730 cm^{-1}. At a 1.0:1.0 ratio, a shoulder appeared on the low frequency side of the absorption band noted above. The intensity of the band at 1730 cm^{-1} was not increased. The X-ray powder pattern of the solid after the 1:1 addition showed it to be a mixture of $MgI_2 \cdot 6THF$ and $Mg(AlH_4)_2 \cdot 4THF$. Further addition of $NaAlH_4$ increased the intensity of the shoulder until at a ratio of 10:1.0 the entire band centered at 1680 cm^{-1}. A yield of 58% for $Mg(AlH_4)_2 \cdot 4THF$ was obtained. The solid at 10:1.0 addition gave the following analysis: Calcd. for $Mg(AlH_4)_2 \cdot 3.8THF$: Mg, 6.75; Al, 15.00; H, 2.22; I, 0.0. Found: Mg, 7.06; Al, 14.93; H, 2.24; I, 0.0. Infrared and X-ray powder pattern data are given in Tables I and III.

B. Reactions of $LiAlH_4$ and MgX_2 in Tetrahydrofuran

(1) Lithium Aluminum Hydride and Magnesium Chloride in Tetrahydrofuran. At a 0.5:1.0 ratio of $LiAlH_4$ in tetrahydrofuran to $MgCl_2$ in tetrahydrofuran, infrared analysis of the clear filtrate showed absorption bands at 1715, 795 and 760 cm^{-1}. At a 1.0:1.0 ratio these bands increased in intensity and broadened somewhat. At a 1.5:1.0 ratio the bands increased in intensity and a shoulder appeared at the low frequency side of the 1715 cm^{-1} band. At a 2.0:1.0 ratio these bands increased in intensity and at a 3.0:1.0 ratio, what was the shoulder in the previous addition became the main band and was centered around 1691 cm^{-1}. The band at 760 cm^{-1} broadened and its intensity increased to a greater extent than the 795 cm^{-1} band. ($LiAlH_4$ in tetrahydrofuran has infrared absorption bands at 1691 cm^{-1} and 763 cm^{-1}). No precipiate was observed even at 3.0:1.0 addition.

In a separate experiment, $LiAlH_4$ was added to $MgCl_2$ in tetrahydrofuran in 1:1 ratio. The solvent was then removed under vacuum and the infrared spectrum and X-ray powder pattern of the resulting solid was obtained. The solid was shown to be a mixture of LiCl and $ClMgAlH_4 \cdot 4THF$.

(2) Lithium Aluminum Hydride and Magnesium Bromide in Tetrahydrofuran. The results obtained were similar to those of the previous system. No precipitate was observed even at $LiAlH_4$ to $MgBr_2$ ratios as high as 5.0:1.0.

(3) Lithium Aluminum Hydride and Magnesium Iodide in Tetrahydrofuran. When $LiAlH_4$ in tetrahydrofuran was added to MgI_2 in tetrahydro-

furan no absorption bands appeared in the infrared spectrum of the solution which were different from those of pure solvent until a $LiAlH_4$:MgI_2 ratio of greater than 2.0:1.0 was attained. At this point absorption bands at 1691 cm^{-1} and 760 cm^{-1} appreared, indicative of $LiAlH_4$ in solution. The precipitation of solid material in this reaction was obscured by the fact that the MgI_2 reactant is insoluble in THF. The X-ray powder diffraction pattern of the solid product showed the compound to be $Mg(AlH_4)_2 \cdot 4THF$. A yield of 85% for $Mg(AlH_4) \cdot 4THF$ was obtained.

C. Reactions of $NaAlH_4$ and MgX_2 in Diethyl Ether

(1) Sodium Aluminum Hydride and Magnesium Bromide in Diethyl Ether. Magnesium bromide in diethyl ether was added to $NaAlH_4$ in diethyl ether in a ratio of 1.0:2.0. The solution was stirred for four days. At the end of this time no bands in the Al-H stretching and deformation regions were found in the infrared spectrum of the solution. An X-ray powder pattern of the solid showed lines due to NaBr and some other compound which was not $MgBr_2$ or $NaAlH_4$. The infrared spectrum of the solid had bands at 1800, 1285, 1190, 1150, 1090, 1045, 995, 895 and 740 cm^{-1}. The white solid was subjected to soxhlet extraction. The infrared spectrum of the resulting solid in nujol exhibited absorption bands at 1800, 1285, 1190, 1150, 1090, 1045, 995, 895 and 740 cm^{-1}. The X-ray powder diffraction pattern is given in Table III. The total yield of $Mg(AlH_4)_2 \cdot 2(C_2H_5)_2O$ was 80%. Anal. Calcd. for $Mg(AlH_4)_2 \cdot 2C_2H_5O$: Mg, 10.37; Al, 23.03; H, 3.41. Found: Mg, 9.43; Al, 23.96; H, 3.50.

D. Reactions of $LiAlH_4$ and MgX_2 in Diethyl Ether

(1) Lithium Aluminum Hydride and Magnesium Chloride in Diethyl Ether. Lithium aluminum hydride in diethyl ether was added to $MgCl_2$ in diethyl ether in a mole ratio of 2.0:1.0. The solution was stirred for two days. The solid obtained gave the following analysis: Found: Cl, 50.43; Mg, 2.96; Al, 7.27. The X-ray powder pattern showed only LiCl. The infrared spectrum of the solid gave no definite bands in the Al-H stretching region. After removing some of the solvent from the filtrate a solid was obtained which gave the following analysis: Found: Cl, 16.17; Mg, 12.53; Al, 24.02; Li, 3.15. The X-ray powder pattern gave lines for LiCl and some other compounds. The infrared spectrum of the solid gave bands at 1845, 1780, 1190, 1150, 1090, 1040, 995 and 900 cm^{-1}.

When $LiAlH_4$ was added to $MgCl_2$ in diethyl ether in a mole ratio of 1.0:1.0, the precipitate obtained gave the following analysis: Found: Cl, 43.91; Mg, 7.25; Al, 11.66; Li, 6.17. The X-ray powder pattern showed lines for LiCl and another compound which didn't correspond to the compound in the 2:1 case. The solid obtained by removing the solvent from the filtrate gave the following analysis: Found: Cl, 22.42; Mg, 12.99; Al, 10.84; Li, 1.27. The X-ray powder pattern gave lines for LiCl. In addition to the lines for LiCl other lines were observed which corresponded to the second solid in the 2:1 case. The infrared spectrum of this solid gave bands at 1800, 1260, 1195, 1150, 1095, 1045, 1000 and 900 cm^{-1}. The solution spectrum of the 2:1 and 1:1 case both gave absorption bands at 1780 cm^{-1} and shoulders on the low frequency side.

(2) Lithium Aluminum Hydride and Magnesium Bromide in Diethyl Ether. At a 0.5:1.0 ratio of $LiAlH_4$ to $MgBr_2$ in diethyl ether, absorption bands at 1780 and 760 cm^{-1} appeared in the infrared spectrum of the solution. At a 1.0:1.0 ratio a shoulder on the low frequency side of the 1780 cm^{-1} band appeared. At a 1.5:1.0 ratio, the bands increased in intensity and the band at 760 cm^{-1} broadened. At a 2.0:1.0 ratio, the bands at 1780 and 1740 cm^{-1} were of equal intensity. At a 3.0:1.0 ratio the bands at 1740 cm^{-1} increased in intensity.

A precipitate was initially formed which gave an indefinite analysis. However, it contained only 2% of the total magnesium.

In a separate experiment, lithium aluminum hydride in diethyl ether was added to $MgBr_2$ in diethyl ether in a mole ratio of 1.0:1.0. The solvent was then removed and a solid obtained. The X-ray powder pattern showed LiBr, but not $LiAlH_4$ or $MgBr_2 \cdot Et_2O$. For the infrared spectrum of the solid in nujol see Table I. Anal. Calcd for LiBr + $BrMgAlH_4 \cdot 2(C_2H_5)_2O$: Li, 1.89; Br, 43.65; Mg, 6.64; Al, 7.37. Found: Li, 1.87; Br, 40.74; Mg, 6.45; Al, 6.45.

(3) Lithium Aluminum Hydride and Magnesium Iodide in Diethyl Ether. No infrared absorption bands other than diethyl ether appeared up to a $LiAlH_4$:MgI_2 ratio of 1.0:1.0. A white solid was obtained up to this ratio which gave the following analysis: Calcd. for $IMgAlH_4 \cdot (C_2H_5)_2O$: I, 49.53; Mg, 9.49; Al, 10.53. Found: I, 49.23; Mg, 9.52; Al, 10.67. Addition of more $LiAlH_4$ gave infrared bands corresponding to $LiAlH_4$. A yield of product was 72%. For the infrared spectrum and X-ray powder diffraction pattern of the solid see Tables I and III.

Reaction of Magnesium Aluminum Hydride and Magnesium Chloride in Tetrahydrofuran

When equimolar amounts of $Mg(AlH_4)_2$ and $MgCl_2$ in THF were mixed, the resulting solution gave an infrared spectrum corresponding to that of $ClMgAlH_4$. The removal of the solvent gave a solid whose infrared spectrum and X-ray powder pattern were identical to $ClMgAlH_4 \cdot 4THF$.

Reaction of Lithium Bromide and Magnesium Aluminum Hydride in Diethyl Ether

When equimolar amounts of LiBr and $Mg(AlH_4)_2$ were mixed in diethyl ether the resulting solution exhibited infrared absorption bands at 1780, 1740 (both of equal intensity), 793 and 762 cm^{-1}. See Figure 1.

CHAPTER III

RESULTS AND DISCUSSION

In the present study $LiAlH_4$ and $NaAlH_4$ were allowed to react with $MgCl_2$, $MgBr_2$ and MgI_2 in diethyl ether and tetrahydrofuran. It is important that these reactions were studied in such detail since the course of the reactions are dependent on the nature of the alkali metal, the halide, the solvent and the solubility of the alkali metal halide by-product. The discussion will be divided roughly into two parts, namely, those combinations of reactants that produce $Mg(AlH_4)_2$ as the reaction product and those combinations of reactants that either stop at the $XMgAlH_4$ stage or produce an equilibrium mixture of products.

$$MAlH_4 + MgX_2 \dashrightarrow MX + XMgAlH_4 \xrightarrow{MAlH_4} MX + Mg(AlH_4)_2 \qquad (6)$$

When $NaAlH_4$ was allowed to react with $MgCl_2$ in tetrahydrofuran in a mole ratio of 1.0:1.0, a white precipitate appeared which was shown by elemental and X-ray powder pattern analyses to be NaCl. The infrared spectrum of the reaction solution showed bands at 1715, 795 and 760 cm^{-1}. None of these bands correspond to $NaAlH_4$, but are in regions characteristic of the Al-H stretching and deformation modes. When this solution was subjected to fractional crystallization, successive fractions gave elemental analyses corresponding to the empirical formula $ClMgAlH_4 \cdot 4THF$. The X-ray powder pattern of this solid shows no lines due to $MgCl_2 \cdot 2THF$, $Mg(AlH_4)_2 \cdot 4THF$, $NaAlH_4$ or NaCl. Furthermore, the infrared spectrum of

this solid shows bands at 1730, 1070, 1030, 920, 880 and 745 cm^{-1} which are not characteristic of either $MgCl_2$ or $Mg(AlH_4)_2 \cdot 4THF$. Also no bands characteristic of Mg-H were observed. It would appear then that the product produced in this reaction is $ClMgAlH_4 \cdot 4THF$ and not a physical mixture of $MgCl_2$ and $Mg(AlH_4)_2$ or $MgCl_2$, MgH_2 and AlH_3.

As one adds more $NaAlH_4$ to the $MgCl_2$ in tetrahydrofuran until the mole ratio is 2.0:1.0, more precipitate is formed and the infrared spectrum of the solution shows no bands in the Al-H or Mg-H stretching and deformation regions. The infrared spectrum of this solid in nujol shows bands at 1725, 1025, 920, 875, 785 and 740 cm^{-1}. The X-ray powder pattern of the solid showed NaCl in admixture with some other compound. The elemental analysis of the solid was consistent with a mixture of NaCl and $Mg(AlH_4)_2 \cdot 4THF$. Soxhlet extraction of this solid with tetrahydrofuran yielded crystals which produced an analysis consistent with $Mg(AlH_4)_2 \cdot 4THF$. The infrared spectrum of the solid extracted product was the same as the original product mixture and the X-ray powder pattern showed all the lines of the mixture after subtracting out the lines due to NaCl. The infrared and powder pattern data of the extracted solid were not consistent with the description of the product as a physical mixture of MgH_2 and AlH_3. Thus it appears clear that the reaction of $NaAlH_4$ and $MgCl_2$ in tetrahydrofuran proceeds stepwise to produce first the soluble $ClMgAlH_4$ and then the insoluble $Mg(AlH_4)_2$.

$$NaAlH_4 + MgCl_2 \xrightarrow{THF} ClMgAlH_4 + NaCl \quad (7)$$

$$ClMgAlH_4 + NaAlH_4 \xrightarrow{THF} Mg(AlH_4)_2 + NaCl \quad (8)$$

When $MgCl_2$ in tetrahydrofuran was added to $Mg(AlH_4)_2 \cdot 4THF$, the insoluble $Mg(AlH_4)_2$ dissolved. The resultant solution produced an infrared spectrum identical to that exhibited by $ClMgAlH_4$. Fractional crystallization of the solution yielded solid fractions whose X-ray powder patterns and infrared analyses were consistent with $ClMgAlH_4 \cdot 4THF$ prepared from $NaAlH_4$ and $MgCl_2$ in 1:1 stoichiometry.

$$MgCl_2 + Mg(AlH_4)_2 \xrightarrow{THF} 2\ ClMgAlH_4 \qquad (9)$$

Since the reaction of $MaAlH_4$ with $MgCl_2$ in tetrahydrofuran is a stepwise reaction to produce $ClMgAlH_4$ and then $Mg(AlH_4)_2$, any $Mg(AlH_4)_2$ formed in the initial stages of the reaction would rapidly redistribute with $MgCl_2$ to form $ClMgAlH_4$. The $Mg(AlH_4)_2$ formed in these reactions was insoluble in tetrahydrofuran, diethyl ether and the common non-protic organic solvents, contrary to the earlier reports by Wiberg.[3-5]

When $NaAlH_4$ was allowed to react with $MgBr_2$ in THF, reactions similar to those with $MgCl_2$ were observed, i.e., at 1:1 ratio $BrMgAlH_4$ was formed and at 2:1 ratio $Mg(AlH_4)_2$ was formed. Since sodium bromide is also insoluble in tetrahydrofuran, $Mg(AlH_4)_2$ produced in this reaction contains two molar equivalents of NaBr.

Magnesium aluminum hydride could be prepared essentially halogen free by reacting $NaAlH_4$ and MgI_2 in tetrahydrofuran at a mole ratio of 10:1.0. Since the NaI by-product is soluble in THF, $Mg(AlH_4)_2$ precipitates from solution halogen free. Attempts to prepare $IMgAlH_4$ in THF were unsuccessful due to the disproportionation of this compound to MgI_2 and $Mg(AlH_4)_2$ in tetrahydrofuran. Since both MgI_2 and $Mg(AlH_4)_2$ are in-

soluble in THF, elemental analysis would not distinguish between a compound of formula $IMgAlH_4$ and a mixture of MgI_2 and $Mg(AlH_4)_2$. Infrared and powder diffraction analyses show that this solid is the physical mixture of MgI_2 and $Mg(AlH_4)_2$.

$$NaAlH_4 + MgI_2 \xrightarrow{THF} NaI + [IMgAlH_4] \dashrightarrow 1/2\ MgI_2\downarrow + 1/2\ Mg(AlH_4)_2\downarrow \quad (10)$$

This disproportionation was demonstrated further by adding $IMgAlH_4 \cdot Et_2O$ to tetrahydrofuran. The reaction was very exothermic and the resultant solid produced an infrared spectrum and X-ray powder pattern consistent with a mixture of $MgI_2 \cdot 6THF$ and $Mg(AlH_4)_2 \cdot 4THF$.

$$2\ IMgAlH_4 + Et_2O \xrightarrow{THF} MgI_2 \cdot 6THF\downarrow + Mg(AlH_4)_2 \cdot 4THF\downarrow + Et_2O \quad (11)$$

A second reaction which produces $Mg(AlH_4)_2$ essentially halogen free is that between $LiAlH_4$ and MgI_2 in tetrahydrofuran at a mole ratio of three or four to one. Here again the disproportionation of $IMgAlH_4$ to MgI_2 and $Mg(AlH_2)_2$ prevents the isolation of $IMgAlH_4$ in THF. The solubility of the LiI by-product enables the $Mg(AlH_4)_2$ to be obtained halogen free.

$$2\ LiAlH_4 + MgI_2 \xrightarrow{THF} Mg(AlH_4)_2 + 2\ LiI \quad (12)$$

When $NaAlH_4$ was allowed to react with $MgBr_2$ in diethyl ether at a mole ratio of 2.0:1.0 a white precipitate formed. This solid was shown by X-ray powder diffraction and infrared data to be a mixture of NaBr and $Mg(AlH_4)_2$.

$$2\ NaAlH_4 + MgBr_2 \xrightarrow{Et_2O} Mg(AlH_4)_2 + 2\ NaBr \qquad (13)$$

Thus it is possible to prepare $Mg(AlH_4)_2$ in both tetrahydrofuran and diethyl ether using the specific combination of reagents described.

The reactions described until now have been reasonably straight forward. When the alkali metal aluminum hydrides were added to the MgX_2 in 1:1 stoichiometry, $XMgAlH_4$ was formed. Upon addition of more $MAlH_4$, the $XMgAlH_4$ reacted further to form $Mg(AlH_4)_2$. In most of these cases the insolubility of the alkali metal halide by-product or of the MgI_2 seems to play an important role. If now we concentrate on the reactions where the alkali metal halide by-product is soluble, we see that the reaction proceeds in a somewhat different fashion.

When $LiAlH_4$ was allowed to react with $MgCl_2$ in tetrahydrofuran in 1.0:1.0 ratio, the reaction filtrate exhibited infrared absorption bands corresponding to $ClMgAlH_4$ as was observed in the reaction of $MgCl_2$ with $NaAlH_4$ in tetrahydrofuran. No precipitate formed in the reaction since LiCl is soluble in tetrahydrofuran. When the 1.0:1.0 ratio of reactants was exceeded, the bands due to $ClMgAlH_4$ didn't decrease in intensity as in the previous cases. Instead as more $LiAlH_4$ was added, bands due to the $LiAlH_4$ increased in intensity. Thus, instead of $Mg(AlH_4)_2$ being produced, an equilibrium resulted as shown in Eq. 14.

$$LiAlH_4 + MgCl_2 \underset{}{\overset{THF}{\rightleftharpoons}} ClMgAlH_4 + LiCl \qquad (14)$$

In order to determine if $ClMgAlH_4$ was the actual intermediate being formed, $LiAlH_4$ was added to $MgCl_2$ in tetrahydrofuran in a 1:1 ratio. The solution was then fractionally crystallized and the resulting solids

subjected to X-ray, infrared and elemental analyses. All of the analyses showed that $ClMgAlH_4 \cdot 4THF$ and LiCl were the major products present.

Similar results were obtained when $LiAlH_4$ and $MgBr_2$ were allowed to react in tetrahydrofuran. The products of this reaction are $BrMgAlH_4 \cdot 4THF$ and LiBr. Here no solid was formed in the reaction even when the $LiAlH_4$:$MgBr_2$ ratio was 5.0:1.0, once again indicating the lack of formation of $Mg(AlH_4)_2$ (insoluble in tetrahydrofuran). Lithium bromide is soluble in tetrahydrofuran.

$$LiAlH_4 + MgBr_2 \overset{THF}{\rightleftharpoons} BrMgAlH_4 + LiBr \qquad (15)$$

The reaction of $LiAlH_4$ and $MgBr_2$ in diethyl ether previously reported by Wiberg to form $Mg(AlH_4)_2$, also showed this equilibrium behavior. The equilibrium in diethyl ether may not lie as far to the right as in tetrahydrofuran (Eq. 15) since the $LiAlH_4$ appears in the solution spectrum sooner than in tetrahydrofuran. A small amount of initial precipitate was formed, however it was found to contain less than 2% of the total magnesium in the reaction. No additional precipitate was formed even at a $LiAlH_4$:$MgBr_2$ ratio of 3:1. The equilibrium nature of the reaction of $LiAlH_4$ and $MgBr_2$ in diethyl ether was verified by the infrared examination of the reaction solution as the $LiAlH_4$ was added to the $MgBr_2$. Figure I shows that even at a ratio of $LiAlH_4$:$MgBr_2$ of 0.5:1.0, unreacted $LiAlH_4$ is present in the reaction mixture. The Al-H stretching band (1740 cm^{-1}) and the Al-H deformation band (755 cm^{-1}) characteristic of $LiAlH_4$ in diethyl ether increases as the $LiAlH_4$:$MgBr_2$ ratio increases. At the $LiAlH_4$:$MgBr_2$ ratio of 2:1 it is clear that the spectrum represents

a mixture of $BrMgAlH_4$ and $LiAlH_4$ in approximately equal molar quantities, rather than $Mg(AlH_4)_2$ reported by Wiberg (compare spectrum for $Mg(AlH_4)_2 \cdot 2\ Et_2O$ in Figure 2).

In order to test the equilibrium hypothesis an ether solution of LiBr was added to $Mg(AlH_4)_2$ obtained by the reaction of $NaAlH_4$ and $MgBr_2$ in diethyl ether. The resulting solution produced absorption bands of equal intensity at 1780 cm^{-1} and 1740 cm^{-1}. ($LiAlH_4$ in diethyl ether has an absorption band at 1740 cm^{-1} and $BrMgAlH_4$ has an absorption band at 1780 cm^{-1} in diethyl ether.) The infrared spectrum (Figure 2) was consistent with that expected for a mixture of $LiAlH_4$ and $BrMgAlH_4$. The spectrum was also identical with the solution spectrum of the 2.0:1.0 addition product of $LiAlH_4$ to $MgBr_2$.

$$LiBr + Mg(AlH_4)_2 \xrightarrow{Et_2O} BrMgAlH_4 + LiAlH_4 \qquad (16)$$

$$2\ LiAlH_4 + MgBr_2 \rightleftharpoons BrMgAlH_4 + LiBr + LiAlH_4 \qquad (17)$$

In diethyl ether the reaction of $LiAlH_4$ with MgI_2 was found to proceed in a fashion similar to the reaction of $LiAlH_4$ and $MgBr_2$. At a stoichiometry of 1:1, a white solid was obtained which was shown by infrared, X-ray powder diffraction and elemental analysis to be $IMgAlH_4 \cdot Et_2O$. Further addition of $LiAlH_4$ did not produce $Mg(AlH_4)_2$.

$$LiAlH_4 + MgI_2 \xrightarrow{Et_2O} IMgAlH_4 + LiI \qquad (18)$$

The results of the reaction of $LiAlH_4$ and $MgCl_2$ in diethyl ether are somewhat confusing. There is evidence that both $ClMgAlH_4$ and $Mg(AlH_4)_2$

are formed. Both the 1:1 and 2:1 reaction mixture appear to contain $ClMgAlH_4$. In the 2:1 case there is evidence also that some $Mg(AlH_4)_2$ is formed.

Infrared studies in the solid state of the compounds prepared indicate that the degree of covalent bonding between the magnesium and the tetrahydridoaluminate group is dependent upon the degree of solvation. This is especially true in the case of the tetrahydrofuran solvates. Both $Mg(AlH_4)_2$ and $ClMgAlH_4$ are obtained from tetrahydrofuran solution as the tetrakis tetrahydrofuranates. The four tetrahydrofuran solvate molecules probably exist in a tetrahedral arrangement about the magnesium atom. This would increase the size of the cation thereby stabilizing the molecule. The solid state infrared spectrum of $Mg(AlH_4)_2 \cdot 4THF$ and $ClMgAlH_4 \cdot 4THF$ both exhibit single sharp bands (25-50 cm^{-1} half width) at 1725 and 1730 cm^{-1} respectively. Since the bands are not split, the four hydrogens on the AlH_4 group must be equivalent with no bridging. This would be consistent with an ionic model.

On the other hand when two of the tetrahydrofuran solvate molecules are removed from the tetrakis solvate, the infrared spectrum of the resulting solid shows that the Al-H stretching band has moved to a higher frequency and split into two bands at 1785 cm^{-1} and 1730 cm^{-1}. This indicates that the compound has become more covalent, and that there are probably bridging hydrogens as indicated by the two bands. If $Mg(AlH_4)_2$ is completely desolvated, the Al-H stretching frequency shifts to an even higher frequency and remains split with bands at 1855 cm^{-1} and 1830 cm^{-1}.

When $ClMgAlH_4 \cdot 4THF$ is dissolved in benzene and recrystallized, the solid obtained contains only two THF solvate molecules. The infrared spectrum of this solid shows that the Al-H stretching band has shifted to a higher frequency. However, the band is not split, although it is somewhat broad and is centered at 1775 cm^{-1}. Upon complete desolvation the Al-H stretching band again shifts to a higher frequency and this time splits into two bands: 1850 and 1830 cm^{-1}.

These data indicate that upon desolvation $Mg(AlH_4)_2$ and $ClMgAlH_4$ exhibited more covalent character through bridging hydrogens. Lithium aluminum hydride in the solid state, which is considered to be covalent, has two bands in the solid state infrared spectrum at 1770 and 1625 cm^{-1}.

CHAPTER IV

CONCLUSIONS

The reactions of complex metal hydrides with magnesium halides in ether solvents can be understood in terms of the two equilibria shown below.

$$MAlH_4 + MgX_2 \rightleftharpoons XMgAlH_4 + MX$$

$$MAlH_4 + XMgAlH_4 \rightleftharpoons Mg(AlH_4)_2 + MX$$

If MX is insoluble, both reactions proceed to the right and $Mg(AlH_4)_2$ is produced. If MX is soluble and $XMgAlH_4$ is insoluble then the first reaction proceeds to the right and the second reaction does not occur. If MX and $XMgAlH_4$ are both soluble, the first reaction lies to the right and the second reaction primarily to the left.

APPENDIX

Table 1. Infrared Data (Mull Spectra, cm^{-1})

$Mg(AlH_4)_2 \cdot 4THF$	$Mg(AlH_4)_2 \cdot 2THF$	$Mg(AlH_4)_2$
1725 S	1785 S	1855 S
1025 S	1730 S	1830 S
920 W		
875 M		
785 S		
740 S		

$Mg(AlH_4)_2 \cdot 2Et_2O$	$ClMgAlH_4 \cdot 4THF$	$ClMgAlH_4 \cdot 2THF$	$ClMgAlH_4$
1800 S	1730 S	1775 S	1850 S
1285 W	1070 W	1030 M	1830 S
1190 W	1030 M	880 M	
1150 M	920 W	810 M	
1090 M	880 M	745 M	
1045 S	745 S		
995 W			
895 W			
740 S			

$BrMgAlH_4 \cdot 4THF$	$BrMgAlH_4 \cdot Et_2O$	$IMgAlH_4 \cdot Et_2O$
1715 S	1830 S	1800 S
1070 W	1290 W	1285 W
1030 M	1260 W	1190 W
915 W	1190 W	1150 W
875 M	1150 W	1090 M
795 S	1090 M	1050 M
745 S	1040 M	900 M
	1000 W	890 W
	900 W	810 S
	750 S	
	720 S	

Table 2. Infrared Data (Solution Spectra cm^{-1}).

$Mg(AlH_4)_2 \cdot 4THF$	$ClMgAlH_4 \cdot 4THF$	$BrMgAlH_4 \cdot 4THF$
1730 M	1715 S	1725 S
800 W	795 M	795 M
750 M	760 M	760 M
$BrMgAlH_4 \cdot Et_2O$	$LiAlH_4 \cdot Et_2O$	$LiAlH_4 \cdot THF$
1780 S	1740 S	1691 S
760 M	755 M	760 M
$NaAlH_4 \cdot THF$		
1680 S		
772 M		

Table 3. X-ray Powder Patterns. (Main lines).

	d	I/Io		d	I/Io
$Mg(AlH_4)_2 \cdot 4THF$	8.76	MS	$IMgAlH_4 \cdot Et_2O$	11.6	S
	7.22	VS		4.58	S
	5.84	M		3.24	MS
	5.50	M		2.83	MS
	4.13	VS			
	3.82	M	$BrMgAlH_4 \cdot Et_2O$	11.6	S
	3.22	M		10.4	M
				8.9	M
$BrMgAlH_4 \cdot 4THF$	11.7	S		4.6	M
	9.71	M			
	8.04	S	$Mg(AlH_4)_2 \cdot 2Et_2O$	10.5	S
	7.11	S		7.9	M
	6.19	M		5.9	S
	4.385	VS		5.6	W
	3.86	M		5.1	W
				4.03	W
$ClMgAlH_4 \cdot 4THF$	11.5	M		3.85	W
	9.4	M		3.65	W(B)
	8.0	M		3.50	M
	7.0	M		3.25	W
	6.15	M		2.96	W
	5.69	M		2.90	VW
	5.24	M		2.80	VW
	4.75	M		2.75	W
	4.1	S		2.40	W
				2.18	W

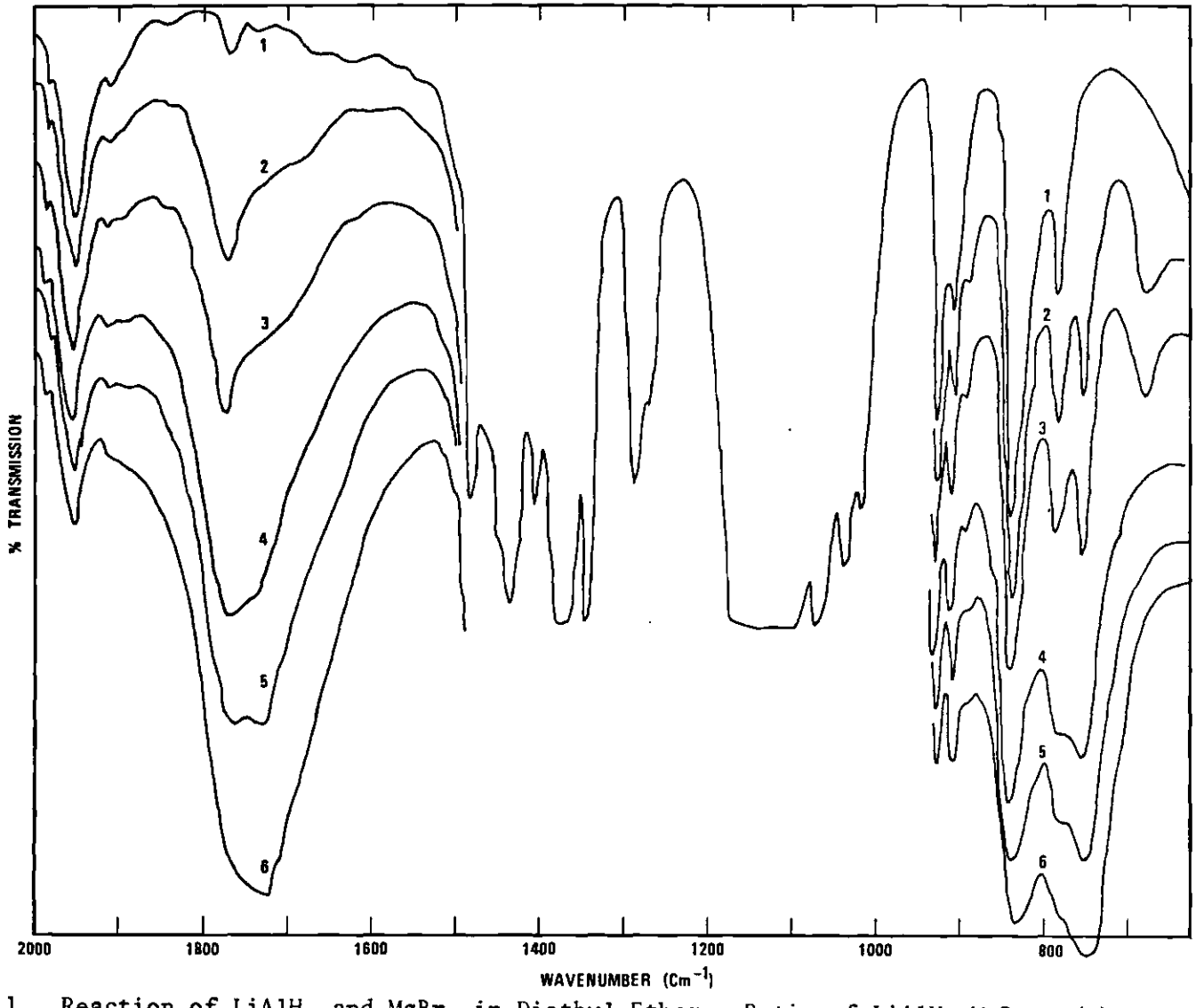

Figure 1. Reaction of $LiAlH_4$ and $MgBr_2$ in Diethyl Ether. Ratio of $LiAlH_4$:$MgBr_2$. (1) Et_2O (2) 0.5:1.0 (3) 1.0:1.0 (4) 1.5:1.0 (5) 2.0:1.0 (6) 3.0:1.0.

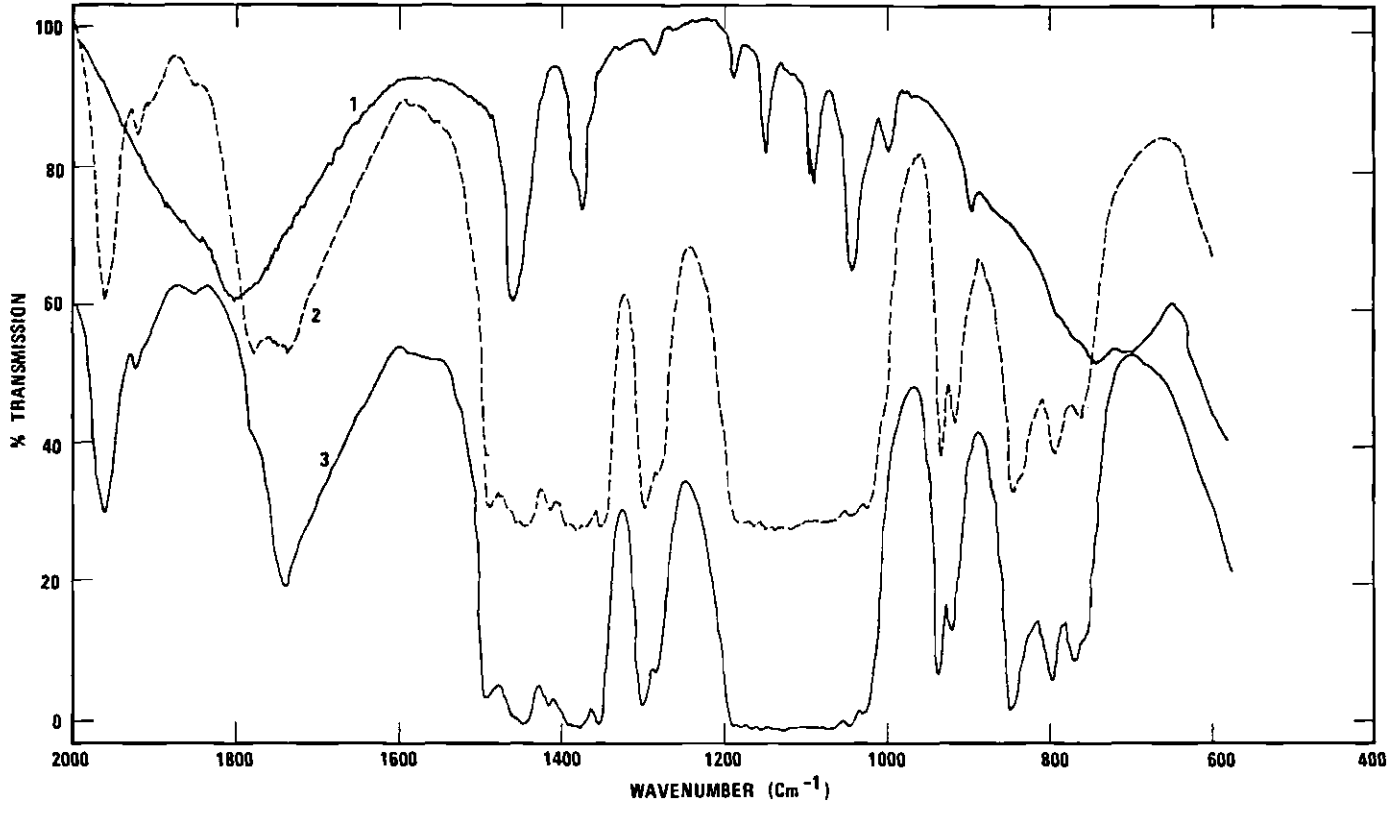

Figure 2. (1) $Mg(AlH_4)_2 \cdot 2Et_2O$ in Nujol (2) $Mg(AlH_4)_2 + LiBr \xrightarrow{Et_2O} LiAlH_4 + BrMgAlH_4$ (3) $LiAlH_4$ in Et_2O.

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PART II

CONCERNING THE REACTIONS OF LITHIUM, SODIUM AND POTASSIUM HYDRIDES WITH MAGNESIUM HALIDES IN ETHER SOLVENTS

CHAPTER I

INTRODUCTION

There are three general methods for preparing magnesium hydride.[1] These methods are represented by the equations shown below (Eqs. 1-3).

$$(C_2H_5)_2Mg \xrightarrow{175^\circ} MgH_2 + 2\ C_2H_4 \quad (1)$$

$$LiAlH_4 + 2\ Mg(C_2H_5)_2 \longrightarrow 2\ MgH_2 + LiAl(C_2H_5)_4 \quad (2)$$

$$Mg + H_2 \xrightarrow[200\ atm]{570^\circ} MgH_2 \quad (3)$$

The pyrolysis of diethyl magnesium[2] (Eq. 1) produces an active form of magnesium hydride which is pyrophoric in air and reacts violently with water and other protic compounds. The reaction of lightium aluminum hydride with diethyl magnesium[3] (Eq. 2) also produces active magnesium hydride. The formation of magnesium hydride from the elements (Eq. 3) occurs at 570° and 200 atm. using magnesium iodide as a catalyst.[4] This method is obviously an economic one and the magnesium hydride prepared by this method is commercially available. Unfortunately MgH_2 prepared by this method is quite unreactive even to air and water.

In 1951 Wiberg,[5] in a short note concerning the preparation of BeH_2, made a one sentence statement that excess lithium hydride and magnesium chloride in diethyl ether react to form either magnesium hydride of Li_nMgH_{2+n}. Since a mixture of excess LiH and MgH_2 could not be distinguished from Li_nMgH_{2+n} except by powder diffraction analysis, one cannot be sure what was formed in this reaction and to what extent. No

subsequent report has appeared.

The reaction of alkali metal hydrides with magnesium halides in ether solvents represents a substantially more convenient and economic route to reactive magnesium hydride than the methods now available. Ideally it was hoped that in a particular solvent an insoluble metal hydride would react with a soluble magnesium halide to form insoluble MgH_2 and soluble magnesium halide. Thus active MgH_2 could be easily isolated in a pure form by filtration. We therefore decided to explore the general scope and utility of the reaction, $MH + MgX_2$ where M = Li, Na and K and X = Cl, Br, I in an attempt to produce active magnesium hydride free from the alkali metal halide by-product. We also wished to determine whether Li_nMgH_{2+n} is formed in the reaction of LiH and $MgBr_2$ and, if so, to isolate the compound.

CHAPTER II

EXPERIMENTAL SECTION

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and water[6] or on the bench using typical Schlenk tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

Instrumentation

Infrared spectra were obtained using a Perkin Elmer model 621 High Resolution Infrared spectrophotometer. Cesium Iodide cells were used. Spectra of solids were obtained in nujol which had been dried over sodium wire and stored in a dry box.

X-ray powder diffraction patters were run using a Debye-Scherrer camera of 114.6 mm diameter using CuK_{α} (1.540 Å) radiation with a nickel filter. Single walled capillaries of 0.5 mm diameter were used. These were filled in the dry box and sealed with a microburner.

Reagents

Tetrahydrofuran and diethyl ether (Fisher Certified Reagent) were distilled over sodium aluminum hydride and lithium aluminum hydride, respectively, immediately before use.

Mercuric halides (Baker Analyzed) were dried under vacuum and used without further purification. Triply sublimed magnesium, obtained from Dow Chemical Co., was washed with diethyl ether and dried under vacuum

prior to use.

Sodium hydride was obtained from Alfa Inorganics as a 57% suspension in mineral oil. Potassium hydride was obtained from Alfa Inorganics as a 50% suspension in mineral oil. Lithium hydride was obtained from Alfa Inorganics as a dry powder. t-Butyl lithium in pentane solution was obtained from Foote Mineral Co.

Analytical Procedures

Halogen analysis was carried out by Volhard method. Magnesium analysis was carried out by titration with EDTA. Hydridic hydrogen analysis was carried out by hydrolyzing a weighed sample of the compound on a high vacuum line and transferring the gas to a calibrated measuring bulb with a Toepler pump after passing the gas through a liquid nitrogen trap. Lithium analysis was carried out by flame photometry.

Preparations and Procedures

Preparation of Magnesium Halides in Diethyl Ether and Tetrahydrofuran

Magnesium halides in ether solvents were prepared as described in Part I.

Preparation of Lithium Hydride

To an autoclave (300 ml chamber) was added 150 ml of t-butyl lithium in pentane. The autoclave was then pressurized to 3000 psi with hydrogen and allowed to stir overnight at room temperature. The resulting solution was not filtered and the white solid product was never allowed to become dry. The supernatant liquid showed no activity and analysis of the solid as a slurry in pentane gave a lithium to hydrogen ratio of 1.0:1.0.

Reactions of Alkali Metal Hydrides with Magnesium Halides in Ether Solvents at Room Temperature

Alkali metal hydrides were allowed to react with magnesium halides in diethyl ether and THF at room temperature in order to determine the general extent of the reaction. The results are summarized in Table 1. An example of the general reaction is given below.

To 83.4 ml of magnesium bromide in THF (0.1436 M) was added 1.15 gm of sodium hydride (57% in mineral oil) and the solution stirred for two days. The solution was then filtered and the analysis of the filtrate showed no magnesium or bromide in solution. The infrared spectra and X-ray powder pattern of the solid indicate a mixture of sodium bromide and magnesium hydride.

Reactions of Alkali Metal Hydrides with Magnesium Halides in Ether Solvents at Reflux Temperatures

In order to obtain some idea of the order of reactivity based on solvent, halide or alkali metal, the alkali metal hydrides were allowed to react with the magnesium halides under a set of standard conditions. These conditions involved a 2:1 ratio of alkali metal hydride:magnesium halide and refluxing solvent for five hours. The solutions were then cooled and filtered and the amount of magnesium hydride in the solid was determined by elemental anslysis. The results are summarized in Table 2.

CHAPTER III

RESULTS AND DISCUSSION

In the present study alkali metal hydrides were allowed to react with magnesium halides in THF and diethyl ether.

$$2\ MH + MgX_2 \longrightarrow 2\ MX + MgH_2 \qquad (4)$$

The purpose of this investigation was to study the possibility of reaction of alkali metal hydrides with magnesium halides as a convenient and economic route to active magnesium hydride.

Commercial grade lithium hydride obtained as a dry powder did not react with magnesium bromide in THF at room temperature. Even after stirring at room temperature for several days only the unreacted starting materials were recovered. Under conditions of reflux for 2 days, some reaction did take place as the Mg:Br ratio in solution rose to 1.0:4.16. Since LiBr is soluble in THF, this ratio indicates the removal of magnesium from solution, presumably as insoluble MgH_2.

$$\underset{\text{(insoluble)}}{2\ LiH} + \underset{\text{(soluble)}}{MgBr_2} \xrightarrow{THF} \underset{\text{(insoluble)}}{MgH_2} + \underset{\text{(soluble)}}{2\ LiBr} \qquad (5)$$

In order to obtain a more reactive form of lithium hydride, t-butyl lithium in pentane was hydrogenated at 3000 psi and 25°. Lithium hydride was obtained as a pentane slurry and remained active as long as it was not allowed to become dry. However, reaction of this LiH with

$MgCl_2$ in THF at room temperature afforded only unreacted starting material after two days. The reaction of this active form of LiH with $MgBr_2$ in THF gave MgH_2 in 33% yield after stirring overnight. Since the reaction was not complete some weak lines corresponding to LiH were found along with lines for MgH_2 in the X-ray powder pattern of the solid product.

The main advantage of using LiH is that the lithium halide by-products are soluble in either diethyl ether or THF making separation from insoluble MgH_2 simple. However if one must obtain the LiH from t-butyl lithium then the convenience and economics of the reaction would no longer be an advantage. With this in mind attention was focused on the use of sodium hydride which is inexpensive and is readily available as a 50% dispersion in mineral oil. Since it is sold as a dispersion, the sodium hydride is able to retain its reactivity. Sodium hydride readily reacts with $MgBr_2$ in THF to yield MgH_2. If excess $MgBr_2$ is used, no sodium hydride is found in the solid product, however the MgH_2 product is mixed with two moles of the insoluble NaBr by-product. However for many purposes this will cause no difficulty.

$$2\ NaH + MgBr_2 \longrightarrow MgH_2 + 2\ NaBr \qquad (6)$$

Sodium hydride was found not to react with MgI_2 in THF. This is unfortunate since NaI is soluble in THF and thus pure MgH_2 could be easily isolated. The lack of reactivity is attributed to the insolubility of MgI_2 in THF (MgI_2 forms an insoluble hexa THF etherate). However, sodium hydride was found to react with MgI_2 in diethyl ether. Ninety percent of the diethyl ether insoluble NaI was removed simply by

$$2\ NaH + MgI_2 \longrightarrow MgH_2 + 2\ NaI \qquad (7)$$

stirring the physical mixture of MgH_2 and NaI in THF. One can effect complete removal of the NaI by high speed stirring at room temperature. Potassium hydride was found to react with magnesium iodide in diethyl ether to yield magnesium hydride quantitatively. The KI by-product was removed by extraction with diglyme.

$$2\ KH + MgI_2 \longrightarrow MgH_2 + 2\ KI \qquad (8)$$

In order to obatin some idea of the relative rates of the reactions between alkali metal hydrides and magnesium halides, a series of reactions were run for 5 hr in refluxing solvent. The yield of magnesium hydride was then determined. The results are summarized in Table 2. As can be seen from the table, sodium hydride is more reactive than potassium hydride in THF. The position of lithium hydride in the reactivity scale is not clear since there are two sources of LiH. The relative rates of the halides are Br > Cl > I. The slower rate of the iodide can be understood as due to the insolubility of the $MgI_2 \cdot 6THF$.

In diethyl ether solvent, reaction between alkali metal hydrides and magnesium halides is slower than in THF. The reactivity of halogen is Br > I, however the reactivity of the alkali metal hydride is reversed to K > Na. The reactivity of magnesium chloride with NaH and KH in diethyl ether was not determined since both magnesium chloride and the alkali metal chloride by-product are insoluble in diethyl ether, thus making the yield of MgH_2 difficult to determine. In addition, reaction of mag-

nesium chloride with NaH in THF produced MgH_2 in only 11% yield after 4 days reflux in THF, a solvent in which one of the reactants ($MgCl_2$) is soluble.

There are a number of factors affecting the relative reactivities of the alkali metal hydrides and the magnesium halides. One might expect a simple increase or decrease in reactivity as the alkali metal increases or decreases in electropositivity. However the solubilities and the degree of solvation of the magnesium halides and the alkali metal halides which fluctuate for various temperature and from solvent to solvent will affect the order observed by changing the free energy of the reaction as well as affecting the kinetic path of the reaction. The source of the alkali metal hydride can also affect the relative reactivity as can be seen by the dramatic change between commercial LiH and that prepared from the high pressure hydrogenation of t-butyl lithium.

CHAPTER IV

CONCLUSIONS

The reaction of alkali metal hydrides with magnesium halides in ether solvents provides an excellent method for the preparation of active magnesium hydride in high yield. The reaction of commercial grade lithium hydride with magnesium halides to produce MgH_2 is very slow; however, the reaction using active lithium hydride prepared by hydrogenolysis of t-butyl lithium proceeds at a reasonable rate. Unfortunately generating active lithium hydride by this method is not very convenient. On the other hand, reaction of commercial grade sodium hydride with magnesium bromide in THF provides a rapid and economic method for preparing active magnesium hydride although by-product NaBr is present as well. If pure magnesium hydride is desired, this preparation can be accomplished by reaction of sodium hydride with magnesium iodide in diethyl ether followed by extraction of the by-product NaI with THF. No evidence could be found for compounds of the type Li_nMgH_{2+n}, suggested earlier by Wiberg to be formed in the reaction of lithium hydride with magnesium chloride.

APPENDIX

Table 1. Summary of Results of Reactions of Metal Hydrides with Magnesium Halides in Ether Solvents.

Reactants	Solvent	Reaction Conditions	Yield MgH_2
NaH/MgI_2	$(C_2H_5)_2O$	Room Temp.; 2 days	100% (a)
NaH/MgI_2	$(C_2H_5)_2O$	Reflux; 36 hr	100%
NaH/MgI_2	THF	Room Temp.; 3 days	no reaction
$NaH/MgBr_2$	THF	Room Temp.; 2 days	100%
$NaH/MgCl_2$	THF	Room Temp.; 4 days	20%
$NaH/MgCl_2$	THF	Reflux; 4 days	11%
$LiH/MgCl_2$	THF	Room Temp.; 2 days	no reaction
$LiH/MgBr_2$	THF	Reflux; 2 days	50%
$LiH/MgCl_2$ (b)	THF	Room Temp.; 2 days	no reaction
$LiH/MgBr_2$ (b)	THF	Room Temp.; 1 day	33%
KH/MgI_2	$(C_2H_5)_2O$	Reflux; 1 day	100%
$LiH/MgBr_2$ (b)	THF	Reflux; 12 hr	86%

(a) NaI can be removed by extraction with THF.

(b) LiH prepared by hydrogenation of t-butyl lithium.

Table 2. Relative Reactivity of Alkali Metal Hydrides toward Magnesium Halides[a].

$2\ MH + MgX_2$	Solvent	Yield of MgH_2 (%)
$LiH/MgCl_2$	THF	0 (b)
$LiH/MgBr_2$	THF	0 (b)
$LiH/MgCl_2$	THF	64 (c)
$LiH/MgBr_2$	THF	74 (c)
LiH/MgI_2	THF	15.9 (c)
$NaH/MgBr_2$	THF	15
$KH/MgBr_2$	THF	4.4
$NaH/MgBr_2$	ether	10
$KH/MgBr_2$	ether	19
NaH/MgI_2	ether	2.5

(a) All reactions run in refluxing solvent for 5 hr.

(b) Commercial grade LiH.

(c) LiH prepared by hydrogenolysis of t-butyl lithium.

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PART III

CONCERNING THE EXISTENCE OF $HMgAlH_4$ AND $HMgBH_4$

CHAPTER 1

INTRODUCTION

The preparation of compounds of the type $HMBH_4$ and $HMAlH_4$ have been investigated previously. In 1940 Burg and Schlesinger[1] reported the preparation of $HBeBH_4 \cdot N(CH_3)_3$ by borane extraction of $Be(BH_4)_2$ with trimethyl amine.

$$Be(BH_4)_2 + 2[N(CH_3)_3] \longrightarrow HBeBH_4 \cdot N(CH_3)_3 + BH_3N(CH_3)_3 \qquad (1)$$

In 1951 Schlesinger[2] and coworkers reported that the addition of diethylmagnesium to a large excess of lightium aluminum hydride in diethyl ether followed by addition of benzene resulted in the precipitation of a solid with the empirical formula $HMgAlH_4$. The compound was not characterized further.

$$LiAlH_4 + Mg(C_2H_5)_2 \longrightarrow HMgAlH_4 + \text{other products} \qquad (2)$$

A recent reinvestigation of the reaction of $LiAlH_4$ with $Mg(C_2H_5)_2$[3] has shown that $HMgAlH_4$ is not produced in this reaction.

The purpose of this work was to examine several possible routes for the synthesis of $HMgAlH_4$ and $HMgBH_4$.

CHAPTER II

EXPERIMENTAL SECTION

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and water[4] or at the bench using typical Schlenk tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

Instrumentation

Infrared spectra were obtained in CsI cells using a Perkin Elmer model 621 High Resolution Infrared Spectrophotometer.

X-ray powder diffraction patterns were obtained using a Debye-Scherrer camera of 114.6 mm diameter using CuK_{α} (1.540 A) radiation with a nickel filter. Single walled capillaries of 0.5 mm diameter were used. These were filled in the dry box and sealed with a microburner.

Reagents

Tetrahydrofuran and benzene (Fisher Certified reagent) were distilled over sodium aluminum hydride immediately prior to use. Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum hydride immediately prior to use.

Mercuric halides (Baker Analyzed) were dried under vacuum and used without further purification. Triply sublimed magnesium was obtained from the Dow Chemical Co. It was washed with diethyl ether and dried under vacuum prior to use.

Lithium and sodium aluminum hydride, sodium hydride (57% suspension in mineral oil) and sodium borohydride were obtained from Ventron Metal Hydrides Division.

Magnesium aluminum hydride, chloromagnesium aluminum hydride, iodomagnesium aluminum hydride and magnesium halide[5] were prepared as described in Part I.

Analytical Procedures

Halogen analysis was carried out by the Volhard method. Aluminum and magnesium analyses were carried out by titration with EDTA. Magnesium analysis in the presence of aluminum was carried out by masking the aluminum with triethanolamine. Lithium analysis was carried out by flame photometry. Hydridic hydrogen was analyzed by hydrolyzing a weighed sample of the compound on a high vacuum line and transferring the gas to a calibrated bulb via a Topler pump after passing the gas through a liquid nitrogen trap.

Preparation and Procedures

Preparation of Lithium Hydride

To an autoclave (300 ml chamber) was added 150 ml of t-butyllithium in pentane. The autoclave was then pressurized to 3000 psi and allowed to stir overnight at room temperature. The resulting solution was not filtered and the white solid obtained was not allowed to become dry. The supernatant liquid showed no activity and the analysis of the solid as a slurry in pentane gave a lithium to hydrogen ratio of 1.00:1.00.

Preparation of tri-n-Butyltin Hydride

To 15 ml of neat disobutylaluminum hydride at 0° was added drop-

wise 10 ml of tri-n-butyltin chloride. After the addition was completed, the ice bath was removed and the reaction mixture allowed to worm slowly to room temperature. The tri-n-butyltin hydride was then distilled from the reaction mixture at 70°/6 mm. The infrared spectrum of the neat compound showed an absorption at 1810 cm^{-1} characteristic of tri-n-butyltin hydride.

Preparation of Chloromagnesium Borohydride

Chloromagnesium borohydride was prepared as described previously.[6] To 75 ml of magnesium chloride in tetrahydrofuran (0.3258 M) was added 0.9234 gm of sodium borohydride. The solution was then stirred for two days. The analysis of this solution gave a Mg:Cl ratio of 1.00:1.04. The infrared spectrum in tetrahydrofuran showed B-H absorptions at 2380 and 2175 cm^{-1}.

Preparation of Ethyl and sec-Butylmagnesium Borohydride

Ethyl magnesium borohydride was prepared as described previously.[5] In the preparation of sec-butyl-magnesium borohydride 2.41 gm of sodium borohydride was added to 50 ml of sec-butylmagnesium chloride in $(C_2H_5)_2O$ (1.09 M). This was diluted with 50 ml of diethyl ether. The solution was stirred for two days. The solution was filtered and the analysis of the filtrate gave a Mg:Cl ratio of 1.0:0.02. The infrared spectrum of the solution showed bands at 2420, 2220, and 535 cm^{-1}.

Prepartion of Hydridomagnesium Ethyltrihydridoaluminate

To 50.58 ml of ethylmagnesium chloride in diethyl ether (1.379 M) was added 50 ml of diethyl ether. To this was added dropwise 100 ml of a solution of lithium aluminum hydride in diethyl ether (0.6976 M) so that the reaction mixture did not become warm. The resulting solution

was filtered and the filtrate gave the following analysis: Mg:Al:Cl; 1.00:1.05:0.1. The infrared spectrum of the solution showed a broad band centered around 1750 cm^{-1} with a shoulder at 1685 cm^{-1}. The X-ray spectrum of the solid obtained from the filtration showed it to be lihtium chloride.

Preparation of Hydridomagnesium n-Butyltrihydridoaluminate

To 45.06 mole of lithium aluminum hydride was added 150 ml of diethyl ether. To this was added 28.71 ml of n-butylmagnesium chloride in diethyl ether (1.564 M). The solution was stirred overnight at room temperature. The solution was filtered and the filtrate gave the following analysis: Mg:Al:Cl; 1.0:1.02:0.1. The infrared spectrum of the filtrate gave bands at 1765, 780 and 680 cm^{-1} (sh).

Reaction of Sodium Hydride and Chloromagnesium Aluminum Hydride in Tetrahydrofuran

To 50 ml of chloromagnesium aluminum hydride in THF (0.2056 M) was added 454.5 mg sodium hydride (57% dispersion in mineral oil). The solution was stirred for two days. The solution was then filtered and the filtrate gave on analysis a Cl:Mg:Al ratio of 0.0:1.0:1.88. From the filtration was isolated 1.9601 gm of solid. The infrared spectrum of the solid gave bands at 1725, 1025, 975, 790 and 745 cm^{-1}. The X-ray powder pattern of the solid gave lines corresponding to sodium chloride, magnesium aluminum hydride and magnesium hydride.

Reaction of Lithium Hydride and Iodomagnesium Aluminum Hydride in Diethyl Ether

To iodomagnesium aluminum hydride was added excess lithium hydride as a slurry in pentane. The solution was stirred for several days.

Elemental analysis of the filtrate gave an I:Mg:Al ratio of 0.52:0.0:1.00. The infrared spectrum of the solution showed bands at 1740 cm^{-1} and 760 cm^{-1}. The solid obtained from the filtration of the reaction mixture gave an infrared spectrum and an X-ray powder pattern characteristic of magnesium hydride.

Reaction of Sodium Hydride and Chloromagnesium Borohydride in Tetrahydrofuran

To 45 ml of chloromagnesium borohydride in THF (0.4887 M) was added 1.9254 gm of sodium hydride (57% dispersion in mineral oil). The solution was stirred for two days and then filtered. The infrared spectrum of the filtrate showed no bands other than those assigned to THF. The X-ray powder pattern of the solid resulting from the filtration gave lines corresponding to sodium chloride, sodium borohydride and magnesium hydride. The infrared spectrum of the solid gave bands corresponding to sodium borohydride and magnesium hydride.

Reaction of Lithium Hydride and Chloromagnesium Borohydride in Tetrahydrofuran

To 50 ml of chloromagnesium borohydride in tetrahydrofuran (0.3257 M) was added 9 ml of a lithium hydride slurry in pentane (approx. 1.6 m). The solution was stirred for several days. The solution was then filtered and an analysis of the filtrate gave a Mg:Cl ratio of 1.0: 1.07.

Reaction of Chloromagnesium Aluminum Hydride and Sodium Hydride in Tetrahydrofuran in the Presence of Triethylamine

To 75 ml of chloromagnesium aluminum hydride in tetrahydrofuran (0.2345 M) was added 10 ml of neat triethylamine and 790 mg of sodium

hydride (57% in mineral oil). The solution was stirred for two days and then filtered. The analysis of the filtrate gave a Mg:Al:Cl ratio of 0.7:0.5:1.1. This represented approximately 70% reaction. The infrared spectrum of the solution showed a band at 1720 cm^{-1}. The infrared spectrum of the solid obtained from filtration showed bands at 1725, 1025, 920, 875, 785 and 740 cm^{-1} indicative of $Mg(AlH_4)_2 \cdot 4THF$.

Reaction of Chloromagnesium Aluminum Hydride and Sodium Hydride in Tetrahydrofuran in the Presence of N,N,N',N' - Tetramethylethylene diamine

To 75 ml of chloromagnesium aluminum hydride in tetrahydrofuran (0.2345 M) was added 11 ml of TMED and 739.6 mg sodium hydride (57% in mineral oil). The solution was stirred for two days and then filtered. This represented about 70% reaction. The infrared spectrum of the solution after filtration had a band at 1715 cm^{-1} corresponding to the Al-H stretching band in chloromagnesium aluminum hydride. The solid obtained from filtration exhibited bands at 1725, 1655, 1025, 1010, 940 (B), 870, 790, 760 and 590 cm^{-1}. The X-ray powder pattern of the solid showed lines corresponding to sodium chloride, magnesium aluminum hydride and magnesium hydride.

Pyrolysis of Hydridomagnesium n-Butyltrihydridoaluminate

To 100 ml of light mineral oil (dried over sodium wire) was added 25 ml of $HMgAlH_3(C_4H_9)$ in diethyl ether (0.34 M). The ether was stripped and the $HMgAlH_3(C_4H_9)$ was found to be insoluble in mineral oil. The mineral oil was then heated to 80° under vacuum for several hours. At the end of this time the reaction was cooled, filtered and washed with benzene. The solid obtained gave an infrared spectrum with bands at 1860 (sh), 1745, 1700 (sh), 920 and 715 cm^{-1}. The analysis of the product gave

a H:Butane:Mg ratio of 4.17:1.0:1.0.

In another experiment the ether was removed from a solution of $HMGAlH_3(C_4H_9)$. The resulting white solid was then heated under vacuum. When the temperature reached 150° the solid began to darken in color and after a few minutes turned gray. At this time some droplets of liquid began to form on the upper end of the flask. The sample was cooled and the solid was washed with hexane and filtered. The resulting filtrate gave the following analysis: Al:Mg:H; 1.45:0.00:1.0. The X-ray powder pattern of the solid obtained from filtration showed lines corresponding to magnesium hydride; aluminum metal; and unreacted $HMgAlH_3(C_4H_9)$. The same results were obtained when $HMgAlH_3(C_4H_9)$ was heated to 150° at atmospheric pressure.

Pyrolysis of Ethylmagnesium Borohydride

The solvent was removed from 25 ml of ethylmagnesium borohydride in THF (2.5 M) and the resulting oil was dissolved in 100 ml of heavy mineral oil. The ethylmagnesium borohydride was missible in the mineral oil. The resulting solution was then heated slowly to a temperature of 170° in an oil bath. At this temperature a gas was evolved and a solid formed. After two hours the solution was allowed to cool to room temperature. The solution was filtered and the solid obtained was washed with benzene. The analysis of the solid gave a Mg:H ratio of 1.0:3.74 and no ethane. The infrared spectrum of the solid showed bands characteristic of magnesium hydride in addition to a band at 2270 cm^{-1} with a shoulder at 2380 cm^{-1}. The X-ray powder pattern showed strong lines corresponding to magnesium hydride.

Pyrolysis of sec-Butylmagnesium Borohydride

Solvent was removed under vacuum from 25 ml of s-butylmagnesium borohydride solution (0.3040 M) in diethyl ether and to the resulting oil was added 100 ml octane. The solution was heated to 80° under vacuum. The solution was cooled and filtered and the solid obtained exhibited X-ray diffraction lines for magnesium hydride and $Mg(BH_4)_2$. In a separate experiment s-butylmagnesium borohydride was heated to 105° under vacuum in heavy mineral oil. A yellow oil was obtained which was not characterized further.

Hydrogenolysis of Hydridomagnesium n-Butyltrihydridoaluminate in Diethyl Ether

100 ml of 0.1 M $HMgAlH_3(n\text{-}C_4H_9)$ in diethyl ether was added to a 300 ml autoclave. The sample was pressurized to 3000 psi and stirred at 25° overnight. No reaction took place, therefore the autoclave was re-pressurized to 3000 psi and stirred at 50° overnight. A white solid was obtained from this reaction. The solution was filtered and the filtrate gave on analysis a Mg:Al ratio of 1.0:2.33. The infrared spectrum of the filtrate exhibited a band at 670 cm^{-1} with a shoulder at 700 cm^{-1} and a band at 1680 cm^{-1}. The gray solid obtained from the filtration gave on analysis a Mg:Al:H ratio of 1.0:0.3:2.63. The infrared spectrum of the solid corresponded to magnesium hydride and the X-ray powder pattern exhibited lines corresponding to magnesium hydride and aluminum metal.

Hydrogenolysis of sec-Butylmagnesium Borohydride

100 ml of 0.1537 M s-butylmagnesium borohydride in diethyl ether was add-d to an autoclave and pressurized to 2000 psi with hydrogen. Reaction was attempted with stirring overnight at 25°. No reaction was ob-

served. The autoclave was repressurized to 3000 psi and the solution stirred at 50° overnight. The solution was filtered and the infrared spectrum of the filtrate exhibited bands at 2450, 2220, and 540 cm^{-1} (sh). The infrared spectrum of the white solid corresponded to magnesium hydride. No bands were observed between 2000-2500 cm^{-1}. The X-ray powder pattern of the solid exhibited lines for magnesium hydride only. The weight of the solid corresponds to a nearly quantitative yield of magnesium hydride.

A similar experiment was run with benzene as the solvent. The results were similar, namely, a solid was obtained exhibiting an X-ray powder pattern and infrared spectrum corresponding to magnesium hydride. Infrared analysis of the filtrated showed bands at 2450 and 2220 cm^{-1}.

Reaction of Sodium Aluminum Hydride and Hydridomagnesium Tetraethylaluminate

To 3.314 gm of $HMgAl(C_2H_5)_4 \cdot 3THF$ in 50 ml of tetrahydrofuran was added 7.7 ml of sodium aluminum hydride in tetrahydrofuran (1.1115 M) and the solution was stirred for several days, however no solid formed.

Reaction of Tri-n-Butyltin Hydride and Ethylmagnesium Borohydride

To 50 ml of ethylmagnesium borohydride in ether (0.5215 M) was added 5.32 ml of neat tri-n-butyltin hydride. The solution was stirred for several days and then was filtered. The infrared spectrum of the filtrate showed bands at 2420, 2210, and 1800 cm^{-1} corresponding to unreacted $EtMgBH_4$ and $(n\text{-}C_4H_9)_3SnH$. Analysis of the solid obtained from the filtration gave a Mg:H ratio of 1.0:2.3. The X-ray powder pattern of the solid showed lines corresponding to magnesium hydride.

Reaction of sec-Butylmagnesium Borohydride and Tri-n-Butyltin Hydride

To 50 ml of sec-butylmagnesium borohydride in ether (0.7850 M) was added 8.02 ml of neat tri-n-butyltin hydride. The resulting solution was stirred for several days and then filtered. The solid obtained from the filtration gave a Mg:H ratio of 1.0:1.89. The infrared spectrum of the solid showed no bands in the B-H stretching region but did show bands characteristic of magnesium hydride.

Reaction of Hydridomagnesium ethyltrihydridoaluminate and Tri-n-Butyl tin Hydride

To 25 ml of $HMgAlH_3(C_2H_5)$ in ether (0.4881 M) was added 2.3 ml of neat tri-n-butyltin hydride. The solution was stirred for several days. A trace amount of solid was formed at the beginning of the reaction. The amount of solid di not increase with time. Analysis of the solid gave a Mg:Al:H ratio of 1.00:1.24:3.59. The infrared spectrum of the solution showed bands at 1800 and 1750 cm^{-1} (sh).

Reaction of Hydridomagnesium n-Butyltrihydridoaluminate and Tri-n-Butyl-tin Hydride

To 35 ml of $HMgAlH_3(C_4H_9)$ in diethyl ether (0.4764 M) was added 3.4 ml of neat tri-n-butyltin hydride. The solution was sitrred for several days. A trace amount of solid of indefinite composition was obtained upon filtration. The infrared spectrum of the filtrate showed bands a 1800 and 1765 cm^{-1} (sh). This infrared spectrum did not change with time.

Reaction of Lithium Aluminum Hydride and Hydridomagnesium n-Butyltri-hydridoaluminate

To 35 ml of $HMgAlH_3(C_4H_9)$ in diethyl ether (0.7036 M) was added

dropwise 50 ml of $LiAlH_4$ in diethyl ether (0.9522 M). The solution was stirred for several days and then filtered. The trace amount of solid obtained from filtration showed Mg:Al:H ratio of 0.00:1.00:2.80. Removal of the solvent from the filtrate yielded a solid whose X-ray powder pattern corresponded to a physical mixture of $LiAlH_4$ and $HMgAlH_3(C_4H_9)$.

Reaction of Diethylaluminum Hydride and Hydridomagnesium n-Butyltetrahydridoaluminate

To 50 ml of $HMgAlH_3(C_4H_9)$ in diethyl ehter (0.7036 M) was added 60 ml of diethylaluminum hydride in diethyl ether (0.5819 M). The solution was stirred for several days but no solid was formed. The diethyl ether was then removed under vacuum at room temperature. The solid obtained was then heated to 80° under vacuum. At this temperature a clear colorless liquid distilled from the reaction mixture. When the distillation stopped, the solid remaining was allowed to cool. Diethyl ether was added to the distillate. The solution containing the distillate showed an Al:H ratio of 1.1:1.0. The infrared spectrum of the distillate showed a band at 1755 cm^{-1}. The solid remaining after solution gave a Mg:Al:H ratio of 1.4:1.0:4.5. The X-ray powder pattern of this solid showed lines due to $HMgAlH_3(C_4H_9)$, MgH_2 and Al metal.

Reaction of Diethylmagnesium and Aluminum Hydride

To 25 ml of diethylmagnesium in tetrahydrofuran (0.5915 M) -80° was added dropwise 53.4 ml of aluminum hydride in tetrahydrofuran (0.4614 M). The solution was stirred for several days and then allowed to warm slowly to room temperature. To the solution was then added hexand precipitating a solid which redissolved upon standing. The tetra-

hydrofuran-hexane mixture was removed under vacuum and fresh hexane added. A solid remained which did not redissolve in hexane. The analysis of this solid gave an Al:H ratio of 1.0:3.5. The hexane solution after filtration gave an Al:H ratio of 1.0:2.04.

Reaction of Sodium Hydride and Magnesium Aluminum Hydride in Tetrahydrofuran

To 75 ml of the THF was added 4.3028 gm of $Mg(AlH_4)_2 \cdot 4THF$ and 677.7 mg of sodium hydride (57% dispersion in mineral oil). The solution was stirred for two days. The solution was then filtered and analyzed. The filtrate contained aluminum but no magnesium. The amount of aluminum in solution corresponded to the amount of sodium hydride added. The infrared spectrum of the filtrate showed bands at 1680 and 772 cm^{-1}. The solid resulting from the filtration exhibited an infrared spectrum with bands at 1725, 1025, 795 and 745 cm^{-1}.

Reaction of Sodium Hydride and Magnesium Borohydride in Diethyl Ether

To 29 ml of magnesium borohydride in diethyl ether (0.3306 M) was added 345 mg of sodium hydride (57% in mineral oil). The solution was stirred for two days and then filtered. The infrared spectrum of the filtrate showed bands at 2440 and 2220 cm^{-1}. The X-ray powder pattern of the solid obtained from the filtration showed lines corresponding to magnesium hydride and sodium borohydride.

Reaction of Magnesium Aluminum Hydride with Trimethyl Amine

Magnesium aluminum hydride (3.29 moles) was added to 20 ml of benzene in a sealed tube reactor. Twenty moles of trimethylamine was added at -196°. The mixture was then sealed under vacuum and the mixture was allowed to stand at room temperature for 10 days. The resulting mixture

was filtered and the analysis of the solid from filtration gave Mg:H ratio of 1.0:1.98. The infrared spectrum and X-ray powder pattern of the solid corresponded to MgH_2. The analysis of the filtrate showed it to contain no Mg but 95 percent of the original aluminum. The infrared spectrum of the filtrate was characteristic of $AlH_3 \cdot 2N(CH_3)_3$.

Pyrolysis of Magnesium Aluminum Hydride

Magnesium aluminum hydride as the monotetrahydrofuran solvate was placed in an aluminia DTA-TGA crucible. The solid was then heated to 145° until the weight loss ceased. The resulting solid was grey in color and its X-ray powder pattern showed lines for MgH_2 and Al metal only.

Reaction of Aluminum Hydride with Magnesium Hydride in Benzene

The solvent was removed from 70 ml of aluminum hydride in tetrahydrofuran (0.3911 M) and to the resulting solid was added 70 ml of benzene. To this solution was added 0.711 g of magnesium hydride. The solution was stirred overnight and filtered. The infrared spectrum of the solution showed weak bands at 1735, 910, and 750 cm^{-1}. The infrared spectrum of the solid obtained from filtration showed bands at 1720, 1025, 915, 875, 785 and 745 cm^{-1}. The X-ray powder pattern of the solid corresponded to $Mg(AlH_4)_2 \cdot 4THF$. Analysis of the solution indicated 88% reaction.

Reaction of Magnesium Hydride and the bis-Trimethylamine Solvate of Aluminum Hydride in Benzene

To 119 mg of magnesium hydride was added 11.85 ml of the bis-trimethylamine solvate of aluminum hydride in benzene (0.3817 M). The solution was stirred for one week. At the end of this time the infrared

spectrum of the solution was unchanged and corresponded to the bis-trimethylamine solvate of aluminum hydride.

CHAPTER III

RESULTS AND DISCUSSION

The reactions employed in the attempt to prepare $HMgAlH_4$ and $HMgBH_4$ can be divided into seven general categories (Eq. 3-9).

$$MH + XMgAlH_4 \longrightarrow MX + HMgAlH_4 \quad (3)$$

$$RMgAlH_4 \xrightarrow{\Delta} HMgAlH_4 + Olefin \quad (4)$$

$$RMgAlH_4 \xrightarrow{H_2} RH + HMgAlH_4 \quad (5)$$

$$RMgAlH_4 + MH \longrightarrow MR + HMgAlH_4 \quad (6)$$

$$Mg(AlH_4)_2 + L \longrightarrow HMgAlH_4 + AlH_3 \cdot L \quad (7)$$

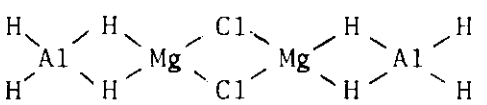
$$MgH_2 + AlH_3 \longrightarrow HMgAlH_4 \quad (8)$$

$$MgH_2 + Mg(AlH_4)_2 \longrightarrow 2\ HMgAlH_4 \quad (9)$$

The first reaction (Eq. 3) involves the reduction of a compound of empirical formula $XMgAlH_4$ or $XMgBH_4$ by a chemical source of hydride ion (eg. NaH). The second method (Eq. 4) involves the pyrolysis of a compound of empirical formula $RMgAlH_4$ or $RMgBH_4$. The third method (Eq. 5) involves the high pressure hydrogenolysis of $RMgAlH_4$ or $RMgBH_4$ compounds. The fourth method (Eq. 6) involves the metathetical exchange between a metal hydrogen compound and $RMgAlH_4$ or $RMgBH_4$. The fifth method (Eq. 7) involves extraction of aluminum hydride from $Mg(AlH_4)_2$. The sixth method (Eq. 8) involves the direct addition of aluminum hydride to MgH_2. The final method (Eq. 9) involves the redistribution of MgH_2 and $Mg(AlH_4)_2$.

$MH + XMgAlH_4$

In an attempt to prepare $HMgAlH_4$ according to Eq. 3, sodium hydride was allowed to react with chloromagnesium aluminum hydride in THF at a molar ratio of 1:1. After several days the solution was filtered. Over 90% of the reaction product was insoluble in the solvent. Elemental analysis of the filtrate gave a Cl:Mg:Al ratio of 0.0:1.0:1.88. The filtrate was thought to consist of a dilute solution of $Mg(AlH_4)_2$. The solid isolated by filtration had an infrared spectrum exhibiting bands at 1725, 1025, 975, 790, and 745 cm^{-1} characteristic of $Mg(AlH_4)_2 \cdot 4THF$. The X-ray powder pattern of the solid confirmed that it was a physical mixture of sodium chloride, magnesium hydride, and magnesium aluminum hydride. The conclusion to be drawn from this experiment depends on the structure of the reactant (dimer $ClMgAlH_4$).[7]



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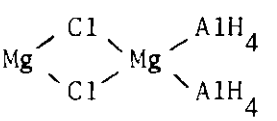

II

If $ClMgAlH_4$ has the structure indicated by I then the conclusion is that $HMgAlH_4$ is produced in the above reaction but disproportionates to MgH_2 and $Mg(AlH_4)_2$.

$$NaH + ClMgAlH_4 \rightarrow NaCl + HMgAlH_4 \rightarrow 1/2\ MgH_2 + 1/2\ Mg(AlH_4)_2 \qquad (10)$$

On the other hand, if $ClMgAlH_4$ was structure II then the conclusion is that MgH_2 and $Mg(AlH_4)_2$ are produced in the above reaction without going through an intermediate $HMgAlH_4$.

In an effort to stabilize $HMgAlH_4$ against disproportionation chloro-

magnesium aluminum hydride was complexed with an amine. Since the possibility of AlH_3 extraction exists, a weak amine was used. In one experiment $ClMgAlH_4$ was first complexed with the chelating amine TMED, however, some aluminum hydride extraction did occur in addition to the formation of $Mg(AlH_4)_2$ and MgH_2.

In another reaction lithium hydride was added in excess as a pentane slurry to iodomagnesium aluminum hydride in diethyl ether. The solution was filtered after several days and the elemental analysis of the filtrate gave a I:Mg:Al ratio of 1.52:0.0:1.0. The infrared spectrum of the filtrate corresponded to lithium aluminum hydride. When the lithium hydride was added to iodomagnesium aluminum hydride in a 1:1 ratio, the infrared spectrum of the solution after stirring for several days corresponded to lithium aluminum hydride. The infrared spectrum and X-ray powder pattern of the solid obtained by filtration of the reaction mixture corresponds to a mixture of lithium iodide, magnesium hydride and unreacted iodomagnesium aluminum hydride. Thus the reaction seems to proceed by both aluminum hydride extraction (Eqs. 11 and 12) and by metathetical exchange followed by disproportionation (Eqs. 13 and 14).

Aluminum Hydride Extraction:

$$LiH + IMgAlH_4 \dashrightarrow LiAlH_4 + IMgH \quad (11)$$

$$2(IMgH) \longrightarrow MgH_2 + MgI_2 \quad (12)$$

Metathetical Exchange:

$$LiH + IMgAlH_4 \dashrightarrow LiI + HMgAlH_4 \quad (13)$$

$$2(HMgAlH_4) \longrightarrow MgH_2 + Mg(AlH_4)_2 \quad (14)$$

$MH + XMgBH_4$

When sodium hydride in excess was allowed to react with chloromagnesium borohydride in THF, the resulting solid was shown by X-ray powder pattern analysis to be a mixture of sodium chloride, sodium borohydride and magnesium hydride. This reaction also presumably proceeded via BH_3 extraction in the presence of excess NAH and/or via metathetical exchange as represented by Equations 15-20.

Boron Hydride Extraction:

$$NaH + ClMgBH_4 \longrightarrow NaBH_4 + HMgCl \quad (15)$$

$$2(HMgCl) \longrightarrow MgH_2 + MgCl_2 \quad (16)$$

$$MgCl_2 + 2(NaH) \longrightarrow MgH_2 + 2\ NaCl^{8} \quad (17)$$

Metathetical Exchange:

$$NaH + ClMgBH_4 \longrightarrow NaCl + HMgBH_4 \quad (18)$$

$$2(HMgBH_4) \longrightarrow MgH_2 + Mg(BH_4)_2 \quad (19)$$

$$Mg(BH_4)_2 + 2\ NaH \longrightarrow 2\ NaBH_4 + MgH_2 \quad (20)$$

However, the overall reaction results in the formation of only NaCl, MgH_2 and $NaBH_4$.

Chloromagnesium borohydride is monomeric in THF.[6] However, the nature of the species in solutionis not known. If the species in solution is $ClMgBH_4$, then $HMgBH_4$ is formed in the reduction with NaH. The $HMgBH_4$ then disproportionates. However, if the species in solution are $MgCl_2$ and $Mg(BH_4)_2$, then reduction with NaH would produce MgH_2 and $Mg(BH_4)_2$ without going through the intermediate $HMgBH_4$.

When lithium hydride was stirred with chloromagnesium borohydride, no reaction was detected after several days.

$$LiH + ClMgBH_4 \xrightarrow{THF} \text{no reaction} \qquad (21)$$

$HMgAlH_3R$ Pyrolysis

In the pyrolysis experiments hydridomagnesium n-butyltrihydridoaluminate [$HMgAlH_3(n\text{-}C_4H_9)$] was suspended in light mineral oil. (For discussion of the nature of $HMgAlH_3R$, see Part IV.) The slurry was heated under vacuum at 80° for several hours, however, only unreacted starting material was recovered. Similar results were obtained in octane solution.

In the compounds represented empirically as $RMgAlH_4$ the alkyl group is actually bonded to aluminum ($HMgAlH_3R$) and is much more stable than if it were bonded to magnesium. With this in mind, higher pyrolysis temperatures were studied. When the solvent was removed under vacuum from an ether solution of $HMgAlH_3(n\text{-}C_4H_9)$ a white solid resulted which was then heated under vacuum. When the temperature reached 150° drops of liquid began collecting on the upper reaches of the flask and the solid began to turn gray. The sample was then cooled, hexane added and the mixture filtered. The filtrate gave an Al:Mg:H ratio of 1.45:0.0:1.0. The X-ray powder pattern of the resulting solid showed lines corresponding to magnesium hydride, aluminum metal and unreacted $HMgAlH_3(n\text{-}C_4H_9)$. These results indicate that before the alkyl group is removed by pyrolysis, the compound $HMgAlH_3R$ decomposes to MgH_2 and $RAlH_2$. However, $RAlH_2$ disproportionates to the more stable R_2AlH and AlH_3 followed by decomposition of AlH_3 to Al, H_2 and intermediate Al-H compounds at 150°.

$$HMgAlH_3R \xrightarrow[\Delta]{} MgH_2 + RAlH_2 \qquad (22)$$

$$2\ RAlH_2 \longrightarrow R_2AlH_4 + AlH_3 \qquad (23)$$

$$AlH_3 \longrightarrow Al + 3/2\ H_2 \qquad (24)$$

The decomposition of $HMgAlH_3R$ in the above manner is not surprising in view of the results of Ziegler and Holzkamp.[9] These workers attempted to distill $Mg[Al(C_2H_5)]_2$ but instead obtained $Al(C_2H_5)_3$ by distillation leaving behind the nonvolatile $Mg(C_2H_5)_2$ (Eq. 25).

$$Mg[Al(C_2H_5)_4]_2 \xrightarrow{\Delta} 2\ Al(C_2H_5)_3 + Mg(C_2H_5)_2 \qquad (25)$$

$RMgBH_4$ Pyrolysis

Ethylmagnesium borohydride was obtained as the THF solvate and was dissolved in 100 ml of heavy mineral oil. This solution was heated slowly to a temperature of 170°. At this point a gas was evolved and a solid formed. The solid obtained was filtered and washed with benzene. Elemental analysis of this solid gave a Mg:H ratio of 1.0:3.54 with no ethane present. The infrared spectrum of the solid exhibited absorption bands at 2270 and 2380 cm^{-1} characteristic of $Mg(BH_4)_2$ as the THF solvate. X-ray powder pattern analysis of the solid exhibited strong lines characteristic of magnesium hydride.

The pyrolysis of sec-butylmagnesium borohydride was attempted since the sec-butyl group is more susceptive to hydrogenolysis at a lower temperature. Sec-butylmagnesium borohydride as the diethyl ether solvate was dissolved in octane and heated to 80° under vacuum. A solid was obtained that exhibited lines in its X-ray powder pattern characteristic of a mixture of magnesium hydride and $Mg(BH_4)_2$.

$HMgAlH_3R$ Hydrogenolysis

The hydrogenolysis of $HMgAlH_3(n\text{-}C_4H_9)$ in diethyl ether was carried out at 3000 psi hydrogen at 50°. The solution was filtered and the ele-

mental analysis of the filtrate gave a Mg:Al ratio of 1.0:2.33. The infrared spectrum of the filtrate gave bands in the Al-C stretching region at 670 cm^{-1} and a shoulder at 700 cm^{-1}, also a band at 1680 cm^{-1}. This combination of absorption bands is characteristic of AlR_2H_2 compounds. The solid obtained from this filtration gave on analysis a Mg:Al:H ratio of 1.0:0.3:2.63. The infrared spectrum of the solid corresponded to magnesium hydride, however, no bands in the Al-H stretching region were observed. The X-ray powder pattern corresponded to magnesium hydride and Al metal. Although hydrogenolysis of an $RMgAlH_4$ compound would be expected to produce $HMgAlH_4$ or a mixture of MgH_2 and $Mg(AlH_4)_2$, only MgH_2 was detected.

The hydrogenolysis of $HMgAlH_3R$ appears to follow a course similar to the pyrolysis of this compound. That is the formation of MgH_2 and $RAlH_2$ followed by disproportionation of the $RAlH_2$ to R_2AlH and AlH_3. The R_2AlH could then react with the MgH_2 formed to give $Mg(AlR_2H_2)_2$. The AlH_3 would decompose to hydrogen and Al metal as indicated by the powder pattern of the solid.

$$HMgAlH_3R \xrightarrow{\Delta} MgH_2 + RAlH_2 \quad (26)$$

$$2\ RAlH_2 \longrightarrow R_2AlH + AlH_3 \quad (27)$$

$$AlH_3 \longrightarrow Al + 3/2\ H \quad (28)$$

$$2\ R_2AlH + MgH_2 \longrightarrow Mg(AlR_2H_2)_2 \quad (29)$$

$RMgBH_4$ Hydrogenolysis

The results of the hydrogenolysis of sec-butylmagnesium borohydride in both diethyl ether and benzene are straight forward. The solid obtained from this reaction in diethyl ether had an infrared spectrum

corresponding to magnesium hydride, while no bands in the boron-hydrogen stretching region were observed. The X-ray powder pattern gave strong lines corresponding to magnesium hydride. The weight of the solid obtained corresponded to a quantitative yield of magnesium hydride. The filtrate from this reaction exhibited infrared bands at 2450 and 2220 cm^{-1} characteristic of $Mg(BH_4)_2$ as the diethyl ether solvate.

$$2(s\text{-}C_4H_9MgBH_4) \xrightarrow{H_2} MgH_2 + Mg(BH_4)_2 + C_4H_{10} \qquad (30)$$

When the reaction was carried out in benzene similar results were obtained. That is, magnesium borohydride (as the ether solvate) in solution and solid magnesium hydride were formed.

In an attempt to learn something of the nature of sec-butylmagnesium borohydride in solution, its molecular association in diethyl ether was measured. The association was found to increase steadily from i = 1.23 at 0.066 molal to i = 1.45 at 0.31 molal. It is clear that hydrogenolysis of this compound does not produce hydridomagnesium borohydride but instead a mixture of magnesium hydride and magnesium borohydride. This result also establishes the point that magnesium hydride and magnesium borohydride will not redistribute in solution to yield hydridomagnesium borohydride.

$$\underline{RMgBH_4 + MH}$$

Ethylmagnesium borohydride in diethyl ether was allowed to react with tri-n-butyltin hydride in a 1:1 mole ratio for several days. At the end of this time, the mixture was filtered. The infrared spectrum of the solution showed bands characteristic of unreacted $EtMgBH_4$ and Bu_3SnH.

The X-ray powder pattern of this solid corresponded to that of magnesium hydride.

In another experiment s-butylmagnesium borohydride in diethyl ether was also allowed to react with tri-n-butyltin hydride in a 1:1 mole ratio. Infrared spectra of the supernatant solution were taken at various intervals. The spectra indicated the disappearance of the Sn-H band at 1800 cm^{-1} and the Mg-C stretching band at 535 cm^{-1}. When these bands had disappeared completely the solution was filtered. The solid obtained by this filtration gave a Mg:H ratio of 1.0:1.89. The infrared spectrum of the solid showed no bands due to B-H stretching but did show bands characteristic of magnesium hydride. Infrared analysis of the filtrate indicated the presence of $Mg(BH_4)_2$.

$$s\text{-}C_4H_9MgBH_4 + (n\text{-}C_4H_9)_3SnH \longrightarrow 1/2\ MgH_2 + 1/2\ Mg(BH_4)_2 + (n\text{-}C_4H_9)_3Sn(s\text{-}C_4H_9) \qquad (31)$$

$HMgAlH_3R$ + MH

Tri-n-butyltin hydride was allowed to react in a 1:1 mole ratio with $HMgAlH_3(C_2H_5)$ in ether and in a separate experiment with $HMgAlH_3(n\text{-}C_4H_9)$. In both cases a trace amount of solid of indefinite composition was formed within a few minutes of initiation of the reaction. However, the amounts of this solid did not increase even after stirring for several days. The infrared spectrum of the solution showed a mixture of unreacted Bu_3SnH and $HMgAlH_3R$. The infrared spectrum of the solution did not change even after stirring for several days. The conclusion is that the $(C_4H_9)_3SnH$ does not react with $HMgAlH_3R$.

Newman and coworkers[10] in the examination of the reaction of trialkyltin hydrides with aluminum alkyls found that ethers and tertiary amines inhibit the reaction. They conclude that the electron deficient state of the aluminum is important in the exchange. Since in the tetrahydroaluminate compounds the aluminum is no longer electron deficient, it is perhaps not surprising that the reaction between $(C_4H_9)_3SnH$ and $HMgAlH_3R$ does not proceed. Van Der Kerk and coworkers[11] in their examination of the reaction between $(C_6H_5)_3SnH$ and $(C_2H_5)MgBr\ N(C_2H_5)_3$ reported that instead of getting hydrogen alkyl exchange, ethane was evolved and a compound with a tin-magnesium bond was formed. It should be emphasized that in none of the reactions between R_3SnH and either $HMgAlH_3R$ or $RMgBH_4$ was any gas evolved.

Diethylaluminum hydride was allowed to react with $HMgAlH_3(n\text{-}C_4H_9)$ in a 1:1 mole ratio in diethyl ether. No solid was formed after stirring the solution for several days. The diethyl ether was then removed under vacuum and the solid obtained was heated under vacuum to 80°. At this point a clear colorless liquid distilled. The analysis of this distillate after diethyl ether was added gave an Al:H ratio of 1.1:1.0. The infrared spectrum of the solution gave a sharp band at 1755 cm^{-1} indicating the presence of $(C_2H_5)_2AlH$. The solid remaining after the distillation was completed gave a Mg:Al:H ratio of 1.47:1.0:4.5. The X-ray powder pattern of the solid showed lines characteristic of $HMgAlH_3(C_4H_9)$, MgH_2 and Al metal.

In this reaction a complex may have been formed between $(C_2H_5)_2AlH$ and $HMgAlH_3R$ which upon heating decomposed again to $(C_2H_5)_2AlH$ and $HMgAlH_3R$. The low aluminum analysis of the solid as well as the presence

of Al metal dn MgH_2 in the powder pattern may be due to a decomposition of the $HMgAlH_3R$ similar to that seen in the pyrolysis experiments.

$$(C_2H_5)_2AlH + HMgAlH_3R \longrightarrow [(C_2H_5)_2AlH\ HMgAlH_3R] \xrightarrow{\Delta} (C_2H_5)_2AlH\uparrow + HMgAlH_3R \qquad (32)$$

Diethylmagnesium was allowed to react with aluminum hydride in THF in a mole ratio of 3:5. It was expected that $Al(C_2H_5)_3$ and $HMgAlH_4$ would be formed according to equation 33. However, no solid was formed

$$3\ Mg(C_2H_5)_2 + 5\ AlH_3 \rightleftharpoons \begin{matrix} 2\ Al(C_2H_5)_3 + 3\ HMgAlH_4 \\ 2(C_2H_5)_2AlH + 3\ HMgAlH_3(C_2H_5 \end{matrix} \qquad (33)$$

initially. The tetrahydrofuran solvent was removed under vacuum and hexane added. The hexane solution was then filtered and the analysis of the filtrate gave an Al:H ratio of 1.0:2.04. The analysis of the resulting solid gave an Al:H ratio of 1.0:3.5. This indicates that equation 33 is not followed but that the alkyl groups are statistically distributed between the aluminum atoms.

When hydridomagnesium tetraethylaluminate in THF was allowed to react with an excess of sodium aluminum hydride no precipitate was formed after stirring for several days. Here again, there is probably a statistical redistribution of the alkyl groups among the aluminum atoms.

$$HMgAl(C_2H_5)_4 + NaAlH_4 \not\longrightarrow HMgAlH_4 + NaAl(C_2H_5)_4 \qquad (34)$$

In the reaction of $HMgAlH_3(C_4H_9)$ with excess lithium aluminum hydride any exchange of alkyl groups should yield $HMgAlH_4$. However, after stirring for several days only a small amount of solid was obtained which contained no magnesium and had an Al:H ratio of 1.0:2.8. A solid obtained by the removal of the solvent from the filtrate gave lines in its powder pattern corresponding to a physical mixture of $LiAlH_4$ and $HMgAlH_3(C_4H_9)$. Thus indicating that $HMgAlH_3(C_4H_9)$ does not undergo exchanges of the butyl group with $LiAlH_4$.

$Mg(AlH_4)_2$ + L

Sodium hydride was allowed to react with $Mg(AlH_4)_2$ 4THF in THF solution. The solution was sitrred for several days and then filtered. The infrared spectrum of the filtrate was identical with an independent sample of $NaAlH_4$. The infrared spectrum of the solid showed it to be a mixture of MgH_2 and $Mg(AlH_4)_2$ 4THF. Equations 35 and 36 are presented to describe the most probable reaction path.

$$NaH + Mg(AlH_4)_2 \longrightarrow NaAlH_4 + HMgAlH_4 \quad (35)$$

$$2\ HMgAlH_4 \longrightarrow MgH_2 + Mg(AlH_4)_2 \quad (36)$$

Dilts and Ashby[12] found that trimethylamine abstracts AlH_3 from $Mg(AlH_4)_2$ in 42% yield after ten days in a sealed tube. In an attempt to determine if the AlH_3 absorption produces $HMgAlH_4$, we allowed trimethylamine to react with $Mg(AlH_4)_2$ in a sealed tube for ten days. At the end of this time we recovered AlH_3 2 NMe_3 in 95% yield. The solid remaining was shown by elemental and infrared analysis and X-ray powder pattern to be MgH_2.

$$Mg(AlH_4)_2 + N(CH_3)_3 \begin{cases} \not\longrightarrow & HMgAlH_4 + AlH_3\ N(CH_3)_3 \\ \longrightarrow & MgH_2 + 2[AlH_3\ 2N(CH_3)_3] \end{cases} \quad (37)$$

In an attempt to desolvate $Mg(AlH_4)_2$ THF, this compound was heated at 140° until all the THF had been removed. Desolvated $Mg(AlH_4)_2$ was desired so that its thermal decomposition could be studied in an effort to effect partial propolysis of $Mg(AlH_4)_2$ to $HMgAlH_4$, aluminum and hydrogen. However, the solid obtained from the desolvation was shown by X-ray powder diffraction to contain MgH_2 and Al metal.

$$Mg(AlH_4)_2 \begin{cases} \overset{\Delta}{\not\longrightarrow} & HMgAlH_4 + Al + 1/2\ H_2 \\ \longrightarrow & MgH_2 + 2\ Al + 3\ H_2 \end{cases} \quad (38)$$

$$\underline{Mg(BH_4)_2 + L}$$

Sodium hydride was allowed to react with $Mg(BH_4)_2$ in diethyl ether in a mole ratio of 1:1. After stirring for several days the solution was filtered. The infrared spectrum of the filtrate was identical with an independent sample of $Mg(BH_4)_2$. The X-ray powder pattern showed lines corresponding to sodium borohydride and magnesium hydride. This indicates that any $HMgBH_4$ formed via borane extraction disproportionated to MgH_2 and $Mg(BH_4)_2$.

$$NaH + Mg(BH_4)_2 \longrightarrow NaBH_4 + HMgBH_4 \quad (39)$$

$$2\ HMgBH_4 \longrightarrow MgH_2 + Mg(BH_4)_2 \quad (40)$$

$MgH_2 + AlH_3$

Magnesium hydride was allowed to react with AlH_3 2THF in benzene. The resulting solution was filtered and the filtrate showed weak bands at 1735, 910, and 750 cm^{-1}. These bands are characteristic of $Mg(AlH_4)_2$ 4THF which is slightly soluble in tetrahydrofuran. The infrared spectrum of the solid obtained from this filtration showed bands corresponding to $Mg(AlH_4)_2$ 4THF and MgH_2. The X-ray powder pattern of the solid showed lines corresponding to $Mg(AlH_4)_2$ 4THF. It is very probable that in this case $HMgAlH_4$ is formed. However, it is not clear whether the $Mg(AlH_4)_2$ actually isolated in this reaction is a result of the disproportionation of $HMgAlH_4$ or simply a result of the further reaction of $HMgAlH_4$ with AlH_3 2THF. Magnesium hydride was found not to react with bis-trimethylamine alane in benzene solution.

$$MgH_2 + AlH_3 \xrightarrow{AlH_3} HMgAlH_4 \xrightarrow{AlH_3} Mg(AlH_4)_2 \qquad (41)$$

Although no specific reaction between MgH_2 and either $Mg(AlH_4)_2$ or $Mg(BH_4)_2$ was studied, it is clear from the results of a number of the reactions described in this paper that MgH_2 does not redistribute with either $Mg(AlH_4)_2$ to give $HMgAlH_4$ or with $Mg(BH_4)_2$ to give $HMgBH_4$.

CHAPTER IV

CONCLUSIONS

Seven general methods have been investigated in attempting to prepare $HMgAlH_4$.

$$MH + XMgAlH_4 \longrightarrow MX + HMgAlH_4$$

$$RMgAlH_4 \xrightarrow{\Delta} HMgAlH_4 + Olefine$$

$$RMgAlH_4 \xrightarrow{H_2} RH + HMgAlH_4$$

$$RMgAlH_4 + MH \longrightarrow MR + HMgAlH_4$$

$$Mg(AlH_4)_2 + L \longrightarrow HMgAlH_4 + AlH_3L$$

$$MgH_2 + AlH_3 \longrightarrow HMgAlH_4$$

$$MgH_2 + Mg(AlH_4)_2 \longrightarrow 2\ HMgAlH_4$$

In none of these cases was $HMgAlH_4$ or $HMgBH_4$ isolated. Instead a physical mixture of MgH_2 and either $Mg(AlH_4)_2$ or $Mg(BH_4)_2$ was obtained.

In all probability, if $HMgAlH_4$ and $HMgBH_4$ were stable compounds, some of the reactions studied should have produced these compounds. It is concluded, therefore, that $HMgAlH_4$ and $HMgBH_4$ are unstable and, if formed as intermediates, disproportionate to MgH_2 and $Mg(AlH_4)_2$ or $Mg(BH_4)_2$.

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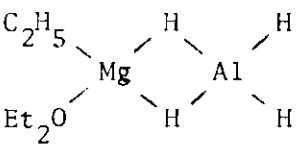
PART IV

CONCERNING THE REACTIONS OF LITHIUM AND SODIUM ALUMINUM HYDRIDE WITH GRIGNARD REAGENTS IN ETHER SOLVENTS

CHAPTER I

INTRODUCTION

Wiberg and Strebel[1] have reported that addition of lithium aluminum hydride to ethyl magnesium chloride in diethyl ether yields a soluble compound with the empirical formula $C_2H_5MgAlH_4$ and the structure assigned to it is shown in I. However, no spectral data were reported to verify this structure.



I

The formation of $C_2H_5MgAlH_4$ can be looked upon as resulting from a simple metathetical exchange reaction involving the formation of stable LiCl as a by-product.

$$C_2H_5MgCl + LiAlH_4 \longrightarrow C_2H_5MgAlH_4 + LiCl \qquad (1)$$

If the product of this reaction has the structure shown in I then this class of compounds represents a good starting point for the preparation of $HMgAlH_4$ by hydrogenolysis (Eq. 2). Hydrogenolysis of R-Mg to H-Mg especially where R = i-C_3H_7 or s-C_4H_9 [2-4] has already been demonstrated.

$$RMgAlH_4 \xrightarrow{H_2} HMgAlH_4 + RH \qquad (2)$$

In 1956 Rice[5] reported that when phenylmagnesium bromide was allowed to react with lithium aluminum hydride in diethyl ether at a mole ratio of 6:1, the resulting product had the empirical formula $(C_6H_5)_2Mg$ C_6H_5MgH $3(C_2H_5)_2O$. When the ratio of Grignard reagent to lithium aluminum hydride was 10:1, a product of empirical formula C_6H_5MgBr C_6H_5MgH $3(C_2H_5)_2O$ was isolated. These compounds were reported to be soluble in benzene and insoluble in diethyl ether. Rice envisioned the reactions as proceeding according to Eq. 3. At the higher Grignard to lithium

$$4\ PhMgBr + LiAlH_4 \longrightarrow 4\ PhMgH + LiBr + AlBr_3 \qquad (3)$$

aluminum hydride ratios PhMgH could complex with the excess Ph_2Mg and PhMgBr in solution giving the products reported.

In attempts to prepare $HMgAlH_4$, $RMgAlH_4$ compounds were prepared according to the method of Wiberg and Strebel. However, hydrogenolysis of the resulting compounds did not product $HMgAlH_4$. Further, inspection of the infrared spectra of the $RMgAlH_4$ compounds showed the absence of absorption in the Mg-C stretching region (500-550 cm^{-1}) which would be expected if $RMgAlH_4$ had the structure shown in I. Furthermore, in the reaction reported by Wiberg and Strebel both of the reactive magnesium species in solution, i.e., R_2Mg and RMgX, should be considered. Since R_2Mg is the more reactive of the R-Mg species in solution, it is not clear that all of the reaction with $LiAlH_4$ should proceed through the RMgX species. In addition it would appear that the hydrogen and R groups could exchange readily in a system such as $RMgAlH_4$ such that rearrangement of $RMgAlH_4$ to $HMgAlH_3R$ might take place readily. $HMgAlH_3R$ would be expected to be the more stable of the two structures since hydrogen

would tend to reside on the more electropositive metal (magnesium).

Previous study of the reaction of $LiAlH_4$ with magnesium halides[6] indicates that a metathetical exchange reaction involving the formation of lithium halide and $Mg\text{-}AlH_4$ compounds (Eq. 4) takes place rather than the type reaction reported by Rice (Eq. 3) in which the AlH_4 group does

$$LiAlH_4 + MgBr_2 \longrightarrow BrMgAlH_4 + LiBr \qquad (4)$$

not maintain its integrity.

Considering these differences in the previous reports concerning such a fundamental reaction and the desire to prepare $RMgAlH_4$ compounds, it was decided to study the reactions of alkali metal aluminum hydrides with Grignard reagents in ether solvents in detail in order to determine the exact course of this reaction.

CHAPTER II

EXPERIMENTAL SECTION

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and water or on the bench using typical Schlenk tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

Instrumentation

Infrared spectra were obtained using a Perkin Elmer Model 621 High Resolution Infrared Spectrophotometer. Cesium Iodide cells were used. X-ray powder diffraction patterns were run using a Debye-Scherrer camera of 114.6 mm diameter using CuK_{α} (1.540 A) radiation with a nickel filter. Single walled capillaries of 0.5 mm diameter were used. These were filled in the dry box and sealed with a microburner.

Reagents

Diethyl ether (Fisher Certified reagent) was distilled over lighium aluminum hydride immediately prior to use. Triply sublimed magnesium was obtained from Dow Chemical Co. The magnesium was washed with diethyl ether and dried under vacuum prior to use. Lithium and sodium aluminum hydride were obtained from Ventron Metal Hydrides Division. Lithium aluminum hydride solutions in diethyl ether were prepared as described in Part I. Sodium aluminum hydride was recrystallized from diethyl ether - THF mixtures.

Analytical Procedures

Halogen analysis was carried out by the Volhard method. Aluminum analysis was carried out by titration with EDTA. Magnesium analysis in the presence of aluminum was carried out by masking the aluminum with triethanolamine and titrating the magnesium with EDTA. Hydridic hydrogen was measured by hydrolyzing a weighed sample on a high vacuum line and transferring the gas to a calibrated bulb via a Topler pump after passing the gas through a liquid nitrogen trap.

Preparations and Procedures

Reaction of Sodium Aluminum Hydride and Methylmagnesium Bromide

To 11.79 moles of sodium aluminum hydride was added 20.68 ml of methyl magnesium bromide in diethyl ether (0.5701 M). The solution was stirred for two days and filtered. The resulting clear filtrate gave on analysis a Mg:Al ratio of 1.0:2.12. The infrared spectrum of the filtrate gave weak bands at 710 and 615 cm^{-1}. The resulting solid gave on analysis a Br:Mg:Al ratio of 1.2:1.0:0.80. These results account for 82.8% of the initial amount of magnesium. The infrared spectrum of the solid gave bands at 1680 cm^{-1} (broad) and 710 cm^{-1} (broad) and also bands corresponding to magnesium hydride.

Reaction of Lithium Aluminum Hydride and Ethylmagnesium Chloride in Diethyl Ether

50.58 ml of ethylmagnesium chloride in diethyl ether (1.379 M) were diluted with 50 ml of ether and then 100 ml of lithium aluminum hydride in diethyl ether (0.6976 M) was added dropwise. The solution was not allowed to become warm enough to reflux the ether. The solution was

then stirred overnight. The solution was then filtered and the analysis of the filtrate gave a Cl:Mg:Al ratio of 1.0:1.0:1.05. The infrared spectrum of the solution showed a broad band at 1750 cm^{-1} with a shoulder at 1685 cm^{-1}.

Reaction of Lithium Aluminum Hydride and n-Butylmagnesium Chloride in Diethyl Ether

To 45.06 moles of lithium aluminum hydride was added 150 ml of diethyl ether. To this solution was added 28.71 ml of n-butylmagnesium chloride in diethyl ether (0.5642 M). The solution was stirred overnight at room temperature. The solution was filtered and 1.6661 gm of solid isolated which gave on analysis: Cl:74.83, Mg:2.98, Al:0.99. The clear filtrate gave the following analysis: Mg:Al:Cl, 1.0:1.02:0.1. The solution contained 95% of the initial amount of magnesium. The infrared spectrum of the filtrate showed bands at 1760 cm^{-1} (broad), 720 cm^{-1} and 680 cm^{-1} (sh). In a separate experiment the solvent was removed from the filtrate and the resulting solid gave an infrared spectrum with bands at 1760 cm^{-1} (broad) and 720 cm^{-1}. The X-ray powder pattern of the solive showed no lines for magnesium hydride. When this solid was dissolved in THF, the resulting infrared spectrum gave bands at 1700, 790, and 755 cm^{-1}.

Reaction of n-Butylmagnesium Bromide with Lithium Aluminum Hydride in Diethyl Ether

To 75 ml of n-butylmagnesium bromide in diethyl ether (0.5786 M) was added slowly 17.89 ml of lithium aluminum hydride in diethyl ether. Shortly after the beginning of the addition a white solid formed. This

solid redissolved shortly after the completion of the addition. The infrared spectrum of the solution showed a broad band around 1760 cm^{-1} and another band at 720 cm^{-1}. The solvent was removed from the reaction mixture and the X-ray powder pattern of the resulting solid corresponded to a physical mixture of LiBr and $HMgAlH_3C_4H_9$.

Reaction of sec-Butylmagnesium Chloride and Lithium Aluminum Hydride in Diethyl Ether

To 10 ml s-butylmagnesium chloride in diethyl ether (2.41 M) was added 14.10 ml of lithium aluminum hydride in diethyl ether (1.698 M). The solution was stirred overnight. The solution was filtered and 1.1582 gm of solid was isolated. The solid on analysis gave a Mg:Al:Cl ratio of 1.0:0.02:0.85. The amount of magnesium contained in the solid represented 65% of the initial magnesium. The infrared spectrum of this solid showed it to contain magnesium hydride. Analysis of the solution gave a Mg:Al ratio of approximately 2.0:3.0.

Reaction of sec-Butylmagnesium Chloride and Sodium Aluminum Hydride in Diethyl Ether

To 10 ml s-butylmagnesium chloride (2.41 M) was added 100 ml di-et-yl ether and 1.3605 gm sodium aluminum hydride. The solution was stirred for two days. The solution was then filtered and the clear filtrate gave on analysis a Mg:Al ratio of 1.0:1.67. The infrared spectrum of the filtrate showed broad bands centered at 1780 cm^{-1} and 720 cm^{-1}. The resulting solid gave on analysis a Mg:Al:Cl ratio of 1.0:0.3:2.0. This represents a 50.8% of the initial amount of magnesium. The infrared spectrum of the solid showed it to contain magnesium hydride.

Reaction of sec-Butyllithium and Iodomagnesium Aluminum Hydride in Cyclohexane

To 100 ml cyclohexane was added 3.5628 gm of $IMgAlH_4$ Et_2O. The slurry was then cooled to 0° and 11.4 ml of sec-butyllithium in pentane (0.24 M) was added. The solution was stirred overnight and allowed to warm slowly to room temperature. The solution was then filtered and analysis of the filtrate gave a Mg:Al ratio of 1.0:1.8. The infrared spectrum of the solid corresponded to magnesium hydride and showed no bands due to Al-H stretching modes. The X-ray powder pattern of the solid corresponded to lithium iodide.

Reaction of Phenylmagnesium Bromide with Lithium Aluminum Hydride in Diethyl Ether

To 50 ml of phenylmagnesium bromide in diethyl ether (1.191 M) was added 50 ml diethyl ether. To the resulting solution was added 24.55 ml of lithium aluminum hydride in ether (2.424 M). During the addition of the lithium aluminum hydride solution some solid was formed and also a brown lower liquid layer. After the addition was completed the solution was stirred overnight. At the end of this time the brown lower liquid layer was gone but a solid remained. The mixture was then filtered and a white solid obtained. Elemental analysis of the solid gave a Mg:H ratio of 1.0:1.94. This represents 48.41% of the initial amount of magnesium added. The infrared spectrum and X-ray powder pattern of the solid showed it to be MgH_2. Analysis of the filtrate gave a Br:Mg:Al ratio of 2.11:1.0:1.91. The infrared spectra of the solution showed a braod band at 1745 cm^{-1}, and also bands at 1245, 895, 770 (B), and 705 cm^{-1}.

Reaction of $HMgAlH_3$ (n-C_4H_9) with Excess Lithium Aluminum Hydride

To 35 ml of $HMgAlH_3$ (n-C_4H_9) in diethyl ether (0.7036 M) was added dropwise 50 ml of lightium aluminum hydride in ether (0.9522 M). A trace amount of solid was formed which contained no magnesium and had an Al:H ratio of 1.0:2.8. The infrared spectrum of the solution corresponded to that of $LiAlH_4$. The solvent was removed under vacuum at room temperature and the resulting solid showed lines in its X-ray powder pattern corresponding to $LiAlH_4$ and $HMgAlH_3$(n-C_4H_9).

Reaction of n-Butylmagnesium Chloride with Excess Lithium Aluminum Hydride

To 20 ml of a diethyl ether solution of $LiAlH_4$ (2.424 M) was added 50 ml diethyl ether. To the resulting solution was added 25 ml of diethyl ether solution of n-butylmagnesium chloride (0.6479 M). The solution was stirred overnight and then filtered. The solid thus obtained was shown by X-ray powder pattern and elemental analysis to be LiCl. The solvent was then removed from the filtrate under vacuum at room temperature. The resulting solid showed lines in its X-ray powder pattern corresponding to a mixture of $LiAlH_4$ and $HMgAlH_3$(n-C_4H_9).

Reaction of Lithium Aluminum Hydride with n-Butylmagnesium Bromide in a Mole Ratio of 1:4

To 100 ml of n-butylmagnesium bromide in diethyl ether (0.5786 M) was added 6 ml of lithium aluminum hydride in ether (2.424 M). The solution was stirred overnight and then filtered. Elemental analysis of the solid gave a Mg:H ratio of 1.0:1.86. The amount of magnesium in the solid corresponded to 46.2% of the initial amount of magnesium. The infrared spectrum and X-ray powder pattern of the solid corresponded to MgH_2.

The infrared spectrum of the filtrate showed a band at 670 cm^{-1} and a shoulder at 615 cm^{-1}. No bands were observed in the Al-H stretching region (2000-1600 cm^{-1}). The solvent was then removed from the filtrate under vacuum at room temperature. Benzene was added to the resulting solid and the mixture stirred overnight. The mixture was then filtered and the analysis of the filtrate gave a Br:Mg:Al:Butane ratio of 1.0: 0.98:1.03:4.28. No hydrogen or lithium were detected in the filtrate and the amount of aluminum in the benzene solution corresponded to 92.54% of the initial amount of aluminum.

In a separate experiment n-butylmagnesium bromide was allowed to react with lithium aluminum hydride in a mole ratio of 4:2.25. At this point all the solid formed initially had redissolved. The infrared spectrum of the solution showed a broad band at 1710 cm^{-1}. The solvent was then removed under vacuum at room temperature and benzene was added. This mixture was then stirred overnight and filtered. The analysis of the filtrate gave a Br:Al:Mg:H ratio of 0.82:1.0:1.71:3.86. This represents 98.4% of the initial amount of aluminum.

Reaction of Phenylmagnesium Bromide with Lithium Aluminum Hydride at a Mole Ratio of 6:1

To 50 ml of phenylmagnesium bromide in diethyl ether (1.191 M) was added 50 ml ether. To this solution was added 4.09 ml of lithium aluminum hydride in ether (2.424 M). During the addition, a tan solid formed and also a brown lower layer. The mixture was stirred for one half hour and then filtered. The solid obtained from filtration was dissolved in benzene and recrystallized by addition of ether. The resulting solid gave a Br:Al:Mg:H ratio of 0.41:0.27:1.79:1.00. Anal.

Calcd. for $(C_6H_5)_2Mg\ C_6H_5MgI\ 3\ O(C_2H_5)_3$:Mg, 9.62; H, 0.198. Found: Mg, 10.24; H, 0.235. The amount of magnesium in the solid corresponded to 16% of the initial amount of magnesium. The infrared spectrum of the solid showed bands at 780, 750, 705, 675, 665, 475, 415, and 390 cm^{-1}.

Reaction of Lithium Aluminum Hydride with n-Butylmagnesium Bromide in Tetrahydrofuran

To 43.4 mmole of n-butylmagnesium bromide was added 75 ml of THF. To the resulting clear solution was added in a dropwise fashion 40.54 ml of $LiAlH_4$ in THF (1.070 M). No solid was formed during the addition and the solution was allowed to stir overnight. The infrared spectrum of the resulting clear solution corresponded to $HMgAlH_3(n\text{-}C_4H_9)$.

Reaction of Sodium Aluminum Hydride with n-Butylmagnesium Bromide in Tetrahydrofuran

To 43.4 mmoles of n-butylmagnesium bromide dissolved in 75 ml of THF was added 26.12 ml of sodium aluminum hydride in THF (1.660 M). The solution was stirred overnight. A solid was formed in the reaction mixture. The solution was filtered and an elemental analysis of the filtrate gave a Br:Mg:Al ratio of 0.0:1.04:1.00. The infrared spectrum of the solution corresponded to $HMgAlH_3(n\text{-}C_4H_9)$. The elemental analysis of the solid gave a Mg:Al ratio of 1.0:1.1. This represented 10% of the initial amount of magnesium. The infrared spectrum of the solid corresponded to $Mg(AlH_4)_2$ 4THF. The X-ray powder pattern of the solid showed lines corresponding to NaBr and $Mg(AlH_4)_2 4THF$.

Infrared Study of the Reaction of Lithium Aluminum Hydride with n-Butylmagnesium Bromide in Diethyl Ether

A 0.4 M solution of n-butylmagnesium bromide in diethyl ether was

placed in a one neck round bottom flask equipped with a side-arm with stopcock. A 2.424 M solution of $LiAlH_4$ was added to this solution in increments via syringe. After each addition the solution was stirred for one half hour and then any solid formed was allowed to settle. A sample for the supernatant solution was then withdrawn via syringe for infrared analysis. At a Grignard to hydride ratio of 1.0:0.0 the following bands were observed: 895, 780, and 540 cm^{-1}. At a Grignard to hydride ratio of 6:1 the 895 and 780 cm^{-1} bands remain the same, but the 540 cm^{-1} band has decreased in intensity and new bands at 670 with a shoulder at 620 cm^{-1} appear. A solid formed at this ratio. At a Grignard to hydride ratio of 4:1 the 895 and 780 cm^{-1} bands are unchanged but the 540 cm^{-1} band has disappeared and the 670 and 620 cm^{-1} bands have increased in intensity and more solid has formed. At a Grignard to hydride ratio of 3:1 the 895 and 780 bands are the same, the 670 and 620 bands have decreased somewhat in intensity but a new band has appeared at 1620 cm^{-1}. The amount of solid doesn't seem to have changed. At a Grignard to hydride ratio of 2:1, the 895 and 780 cm^{-1} bands are unchanged, however, the 670 and 620 cm^{-1} have disappeared a band at 705 cm^{-1} has appeared. The band at 1620 cm^{-1} has disappeared, however, intense band at 1710 cm^{-1} has appeared. At this ratio all the solid has redissolved. At a Grignard reagent:hydride ratio of 1:1, all the solid is still in solution and the solution spectrum show bands at 1760, 895, 780, and 680 cm^{-1}.

Preparation of Isopropoxymagnesium Bromide

To 25 ml of ethyl magnesium bromide in ether (3.016 M) was added 20 ml of ether. The solution was then cooled to 0° and 5.77 ml of neat isopropanol was added slowly. A gas was given off and the solution

stirred overnight. The analysis of the solution gave a Mg:Br ratio of 1.0:1.1.

Reaction of Isopropoxymagnesium Bromide and Lithium Aluminum Hydride

To 75 ml of isopropxymagnesium bromide in diethyl ether (0.2059 M) was added 15.7 ml of lithium alumin-m hydride in ether (0.9811 M). The solution was then stirred overnight and filtered. The analysis of the filtrate gave a Mg:Al:Br ratio of 1.0:1.77:2.04. The infrared spectrum of the solid obtained from the filtration corresponded to magnesium hydride and showed no bands due to Al-H stretching.

Preparation of di-n-Butylaminomagnesium Chloride

To 30 ml of ethylmagnesium chloride in ether (1.149 M) was added 70 ml ether. To this solution was then added 5.8 ml of di-n-butylamine. The solution was then stirred overnight during which time no precipitate formed.

Reaction of di-n-Butylaminomagnesium Chloride and Lithium Aluminum Hydride

To 50 ml of di-n-butylaminomagnesium chloride in ether (0.2981 M) was added 15 ml of lithium aluminum hydride in ether (0.9888 M). The solution was then stirred for two days and filtered. The analysis of the filtrate gave a Mg:Al:Cl ratio of 1.0:1.00:0.0. The infrared spectrum of the solution showed bands at 1830 cm^{-1} (sharp); 870 cm^{-1} and a broad band at 740 cm^{-1}. The compound is also soluble in benzene.

CHAPTER III

RESULTS AND DISCUSSION

An infrared study of the reaction between n-butylmagnesium bromide and lithium aluminum hydride shows that the reaction proceeds by a stepwise exchange of alkyl groups on the magnesium for hydrogen on the aluminum, as shown in Equations 5-9 (see Figure I). Although HMgBr would be an initial product, this compound is known to disproportionate rapidly to MgH_2 and $MgBr_2$ in ether solution.

$$LiAlH_4 + 6\ n\text{-}C_4H_9MgBr \longrightarrow 2\ MgH_2\downarrow + MgBr_2 + LiBr + BrMgAl(n\text{-}C_4H_9)_4 + 2\ n\text{-}C_4H_9MgBr \quad (5)$$

$$LiAlH_4 + 4\ n\text{-}C_4H_9MgBr \longrightarrow 2\ MgH_2\downarrow + MgBr_2 + LiBr + BrMgAl(n\text{-}C_4H_9)_4 \quad (6)$$

$$LiAlH_4 + 3\ n\text{-}C_4H_9MgBr \longrightarrow 3/2\ MgH_2\downarrow + LiBr + 1/2\ MgBr_2 + BrMgAl(n\text{-}C_4H_9)_3 \quad (7)$$

$$LiAlH_4 + 2\ n\text{-}C_4H_9MgBr \longrightarrow MgH_2 + BrMgAlH_2(n\text{-}C_4H_9)_2 + LiBr \quad (8)$$

$$MgH_2 + BrMgAlH_2(n\text{-}C_4H_9)_2 \longrightarrow BrMg_2AlH_4(n\text{-}C_4H_9)_2 \quad (9)$$

$$LiAlH_4 + n\text{-}C_4H_9MgBr \longrightarrow LiBr + (n\text{-}C_4H_9)MgAlH_4 \quad (10)$$

$$n\text{-}C_4H_9MgAlH_4 \longrightarrow HMgAlH_3(n\text{-}C_4H_9) \quad (11)$$

At a ratio of 1.0 $LiAlH_4$ to 6 $n\text{-}C_4H_9MgBr$ (Eq. 5) the infrared band at 540 cm^{-1} characteristic of $n\text{-}C_4H_9MgBr$ has decreased in intensity indicating that some of it has reacted. The band at 670 cm^{-1} with the shoulder at 620 cm^{-1} is characteristic of the AlR_4 group.

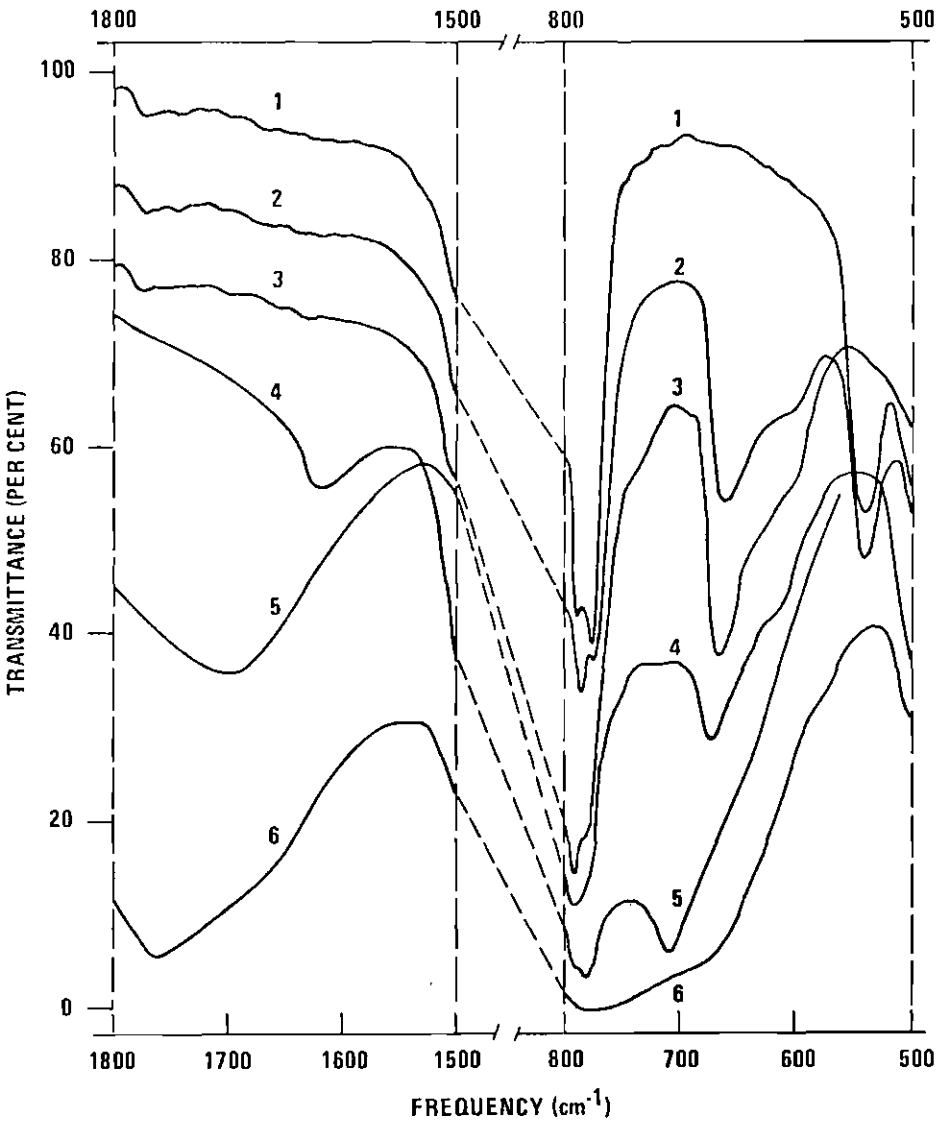


Figure 3. The Reaction of $LiAlH_4$ with n-C_4H_9MgBr in Diethyl Ether. Mole ratio $LiAlH_4$:n-C_4H_9MgBr (1) 0:1; (2) 0.16:1.0; (3) 0.25:1.0; (4) 0.33:1.0; (5) 0.5:1; (6) 1.0:1.0.

At a ratio of 1.0 $LiAlH_4$ to 4.0 n-C_4H_9MgBr (Eq. 6) the band at 540 cm^{-1}, characteristic of n-C_4H_9MgBr has disappeared but the bands at 670 cm^{-1} and 620 cm^{-1} (sh) have increased in intensity. This indicates that all the Grignard reagent has reacted. The solid which began to form in the 6:1 case has now increased. In a separate experiment the solid was isolated by filtration and shown by elemental analysis, X-ray powder pattern and infrared analysis to be MgH_2. The amount of MgH_2 isolated corresponded to a 92.4$ yield accorind to Equation 6. The solvent was then removed from the filtrate and the solid thus obtained was put in benzene and stirred overnight. This was then filtered and the analysis of the solution indicated the presence of a compound of empirical formula $BrMgAl(n\text{-}C_4H_9)_4$. The amount of aluminum in the solution indicated a yield of $BrMgAl(n\text{-}C_4H_9)_4$ of 92% according to Equation 6.

The products of Equation 6 can be envisioned as resultin g from two reaction paths. The first path involves reaction of $LiAlH_4$ with the C-Mg bond of theGrignard reagent according to Equation 12.

$$LiAlH_4 + 4\ n\text{-}C_4H_9MgBr \longrightarrow LiAl(n\text{-}C_4H_9)_4 + 4\ HMgBr$$
$$2\ MgH_2 + 2\ MgBr_2 \qquad (12)$$

The $LiAl(n\text{-}C_4H_9)_4$ thus produced can then react with $MgBr_2$ to yield $BrMgAl(n\text{-}C_4H_9)_4$ according to Equation 13.

$$LiAl(n\text{-}C_4H_9)_4 + MgBr_2 \longrightarrow LiBr + BrMgAl(n\text{-}C_4H_9)_4 \qquad (13)$$

The second path involves the reaction of $LiAlH_4$ with the Mg-Br bond of the Grignard reagent according to Equation 14.

$$LiAlH_4 + 4\ n\text{-}C_4H_9MgBr \longrightarrow LiBr + n\text{-}C_4H_9MgAlH_4 + 3\ n\text{-}C_4H_9MgBr \quad (14)$$

$$n\text{-}C_4H_9MgAlH_4 \longrightarrow HMgAlH_3(n\text{-}C_4H_9) \quad (15)$$

$$HMgAlH_3(n\text{-}C_4H_9) + 3\ n\text{-}C_4H_9MgBr \longrightarrow HMgAl(n\text{-}C_4H_9)_4 + 1.5\ MgH_2 + 1.5\ MgBr_2 \quad (16)$$

$$HMgAl(n\text{-}C_4H_9)_4 + MgBr_2 \longrightarrow BrMgAl(n\text{-}C_4H_9) + 0.5\ MgH_2 + 0.5\ MgBr_2 \quad (17)$$

The $n\text{-}C_4H_9MgAlH_4$ found rearranges to $HMgAl(n\text{-}C_4H_9)_4$ which then reacts with the remaining Grignard reagent according to Equation 16 to yield $HMgAl(n\text{-}C_4H_9)_4$, MgH_2 and $MgBr_2$. The $HMgAl(n\text{-}C_4H_9)_4$ then reacts with $MgBr_2$ according to Equation 17.

At a ratio of 1.0 $LiAlH_4$ to 3.0 $n\text{-}C_4H_9MgBr$ (Eq. 7) the bands at 670 cm^{-1} and 620 cm^{-1} decreased in intensity somewhat and a new band at 1620 cm^{-1} has appeared. The combination of bands between 600-700 cm^{-1} and one at approximately 1600 cm^{-1} was shown[9] to be characteristic of $[AlR_3H]^-$ compounds.

At a ratio of 1.0 $LiAlH_4$ to 2.0 $n\text{-}C_4H_9MgBr$ (Eq. 8) the bands at 670 and 620 cm^{-1} disappeared and a band at 705 cm^{-1} appread. Also the band at 1620 cm^{-1} disappeared, however, an intense band at 1710 cm^{-1} appeared. This combination of bands around 1700 cm^{-1} and 700 cm^{-1} has been shown[9] to be characteristic of the $[AlR_2H_2]^-$ group. Also at this ratio the MgH_2 noted above has all redissolved. In a separate experiment $LiAlH_4$ was added to $n\text{-}C_4H_9MgBr$ in a ratio of 2.25:4.0. The solvent was removed under vacuum and the resulting solid extracted with benzene. Analysis of the benzene solution after filtration gave a Br:Al:Mg:H ratio of 0.82:1.0:1.71:3.86. This ratio can be rationalized as representing a compound of empirical formula $BrMg_2AlH_2(n\text{-}C_4H_9)_2$.

At a ratio of 1.0 $LiAlH_4$ to 1.0 $n\text{-}C_4H_9MgBr$ (Eq. 10) the solution is clear. The infrared spectrum of the solution shows bands at 1760 cm^{-1} and 720 cm^{-1}. This combination of bands has been shown[9] to be characteristic of $[AlH_3R]$ compounds.

When n-butylmagnesium chloride was allowed to react with lithium aluminum hydride in diethyl ether at a mole ratio of 1:1, a solid was obtained which was shown by elemental analysis and X-ray powder pattern analysis to be lithium chloride. Analysis of the filtrate gave a Mg:Al ratio of 1.0:1.02 and the amount of magnesium in solution represented 95% of the original magnesium. The infrared spectrum of thefiltrate showed broad bands at 1760 and 720 cm^{-1} with a shoulder at 680 cm^{-1}. No bands were observed in the Mg-C stretching region (500-535 cm^{-1}). Lithium monoethylaluminate exhibits a broad absorption at 1740 cm^{-1} with a shoulder at 1700 cm^{-1}. This band is very similar in shape and position to the Al-H stretching band at 1760 cm^{-1} exhibited by $HMgAlH_3(n\text{-}C_4H_9)$. Thus,we have concluded that the alkyl group is bonded to the aluminum and not magnesium.

In a separate experiment $LiAlH_4$ was allowed to react with $n\text{-}C_4H_9MgBr$ in a 1.0:1.0 ratio. The solution spectrum was identical to that observed earlier in the infrared study when the ratio of $LiAlH_4$:$n\text{-}C_4H_9MgBr$ was 1:1. The solvent was removed from the reaction mixture and the X-ray powder pattern showed lines corresponding to LiBr plus other lines corresponding to the $HMgAlH_3(n\text{-}C_4H_9)$ isolated from the 1:1 addition of $n\text{-}C_4H_9MgCl$ to $LiAlH_4$ discussed above.

When $HMgAlH_3(n\text{-}C_4H_9)$ was dissolved in THF the major absorption bands in the infrared shifted to 1700, 790 and 755 cm^{-1}. Still in THF no bands

are observed in the 500-535 cm^{-1} region characteristic of a C-Mg compound, so that the butyl group is also presumed to be attached to aluminum in THF solution.

When lithium aluminum hydride was allowed to react with ethylmagnesium chloride in diethyl ether at a mole ratio of 1:1, a solution was obtained which after filtration was shown by elemental analysis to have a Cl:Mg:Al ratio of 0.1:1.00:1.05. The infrared spectrum of the solution exhibited an absorption band at 1750 cm^{-1} with a shoulder at 1685 cm^{-1}. It is important to note that if the reaction was allowed to become too vigorous, the initially formed $HMgAlH_3C_2H_5$ disproportionated to MgH_2 and $Mg(AlH_3C_2H_5)_2$. In the case of the formation of $HMgAlH_3(n\text{-}C_4H_9)$, no evidence of disproportionation was observed even under reflux conditions.

$$LiAlH_4 + C_2H_5MgCl \xrightarrow[\text{temperature}]{\text{room}} LiCl + HMgAlH_3C_2H_5 \qquad (18)$$

$$LiAlH_4 + C_2H_5MgCl \xrightarrow{\text{ether reflux}} LiCl + 1.2\ MgH_2 + 1/2\ Mg(AlH_3C_2H_5)_2 \qquad (19)$$

It was desirable to prepare methylmagnesium aluminum hydride by the reaction of sodium aluminum hydride with methylmagnesium bromide in diethyl ether in order to study the low temperature NMR of the resulting product for structure elucidation purposes. However, a solid was obtained from this reaction which had a Br:Mg:Al ratio of 1.2:1.0:0.80. The infrared spectrum of the solid exhibited bands at 1680 (broad and 710 cm^{-1} (broad) and also bands corresponding to magnesium hydride. The analysis of the solution obtained from this reaction by filtration of the

solid gave upon elemental analysis a Mg:Al ratio of 1.0:2.12. The conclusion is that the $HMgAlH_3(CH_3)$ is unstable and disproportionates to MgH_2 and $Mg(AlH_3(CH_3)_2$ at room temperature.

$$NaAlH_4 + CH_3MgBr \longrightarrow NaBr + HMgAlH_3CH_3 \quad (20)$$

$$2\ HMgAlH_3CH_3 \longrightarrow MgH_2 + Mg(AlH_3CH_3)_2 \quad (21)$$

Sodium aluminum hydride was allowed to react with s-butylmagnesium chloride in diethyl ether in a 1:1 mole ratio. The solution obtained by filtration gave upon elemental analysis a Mg:Al ratio of 1.0:1.67. The infrared spectrum of the filtrate showed broad bands at 1780 and 720 cm^{-1}. The solid resulting from this filtration gave a Mg:Al:Cl ratio of 1.0:0.3:2.0. This solid represented 50.8% of the initial amount of magnesium. The infrared spectrum of the solid showed bands corresponding to magnesium hydride but no bands were observed characteristic of the Al-H stretching region. Similar results were obtained in the reaction of lithium aluminum hydride with sec-butylmagnesium chloride. The conclusion is similar to that arrived at earlier in the reaction of $NaAlH_4$ with methylmagnesium bromide, that is, the initial product $[HMgAlH_3(s\text{-}C_4H_9)]$ disproportionates to MgH_2 and $Mg(AlH_3s\text{-}C_4H_9)_2$ under the conditions of the reaction.

$$NaAlH_4 + s\text{-}C_4H_9MgCl \longrightarrow HMgAlH_3\ (s\text{-}C_4H_9) \quad (22)$$

$$2\ HMgAlH_3(s\text{-}C_4H_9) \longrightarrow MgH_2 + Mg[AlH_3(s\text{-}C_4H_9)]_2 \quad (23)$$

In an effort to prepare sec-butylmagnesium aluminum hydride by an alternate route, sec-butyllithium was allowed to react with iodomagnesium aluminum hydride in a 1:1 mole ratio in cyclohexane at 0°. After

the reaction mixture was filtered, analysis of the filtrate gave a Mg:Al ratio of 1.0:1.8. The infrared spectrum of the solid corresponded to magnesium hydride and showed no bands due to the Al-H stretching mode. The X-ray powder pattern showed the solid to contain lithium iodide. The conclusion is that a metathetical exchange reaction occurs producing LiI and $s\text{-}C_4H_9MgAlH_4$ which then rearrange to $HMgAlH_3s\text{-}C_4H_9$ and subsequently disproportionates to MgH_2 and $Mg(AlH_3s\text{-}C_4H_9)_2$.

$$s\text{-}C_4H_9Li + 1MgAlH_4 \longrightarrow LiI + HMgAlH_3\ (s\text{-}C_4H_9) \quad (24)$$

$$2\ HMgAlH_3(s\text{-}C_4H_9 \longrightarrow MgH_2 + Mg[AlH_3(s\text{-}C_4H_9)]_2 \quad (25)$$

When $LiAlH_4$ was allowed to react with phenylmagnesium bromide at a mole ratio of 1:6 the physical observations corresponded to those reported by Rice,[5] that is, a solid was formed in the reaction and a brown lower layer appeared. The solid was dissolved in benzene and recrystallized by addition of diethyl ether. Analysis of this solid gave a Br:Al:Mg:H ratio of 0.41:0.27:1.79:1.0. The weight percent found for Mg, 10.24 and H, 0.235 are not far from those reported by Rice (Mg, 9.62 and H, 0.195). Rice attributes this analysis to $(C_6H_5)_2Mg\cdot C_6H_5MgH\cdot 3[O(C_2H_5)_2]$. The infrared spectrum of the solid obtained from the recrystallization had bands at approximately 700 cm^{-1} characteristic of monosubstituted phenyl groups. There were no bands between 500-600 cm^{-1}, however, there was a band at 480 cm^{-1} which could be attributed to Mg-C stretching. No evidence of $LiAlBr_4$ was found however analysis of the lower layer produced in the reaction after extraction with benzene did give an Al:Br atio of 1.0:1.0 with magnesium present in excess indicating the possibility of $BrMgAl(C_6H_5)_4$ as observed in the 6:1 case for

the reaction of $n\text{-}C_4H_9MgBr$ with $LiAlH_4$. The $(C_6H_5)_2Mg \cdot C_6H_5MgH \cdot 3[O(C_2H_5)_2]$ reported by Rice could be envisioned as resulting from the following sequence of reactions.

$$2\ C_6H_5MgBr \rightleftharpoons (C_6H_5)_2Mg + MgBr_2 \tag{26}$$

$$4(C_6H_5)_2Mg + LiAlH_4 \longrightarrow 4(C_6H_5MgH) + LiAl(C_6H_5)_4 \tag{27}$$

$$(C_6H_5)_2Mg + C_6H_5MgH \longrightarrow (C_6H_5)_2Mg \cdot C_6H_5MgH \tag{28}$$

The Schlenk equilibrium for C_6H_5MgBr in either (Eq. 26) has an equilibrium constant approximately equal to 0.25. When $LiAlH_4$ is added to phenyl magnesium bromide, it is reasonable that reaction takes place between $LiAlH_4$ and $(C_6H_5)_2Mg$ to form C_6H_5MgH which is then stabilized by reaction with $(C_6H_5)_2Mg$ to form a complex. Recently similar complexes ($RMgH \cdot R_2Mg$) have been prepared where R=CH_3, $n\text{-}C_4H_9$ and C_6H_5 by the hydrogenolysis of unsymmetrical dialkylmagnesium compounds.[10]

$$2(RMgR') \xrightarrow[\Delta]{H_2} RMgH \cdot RMgR' + R'H \tag{29}$$

The formation $BrMgAl(C_6H_5)_4$ in the reaction of $LiAlH_4$ with $(C_6H_5)_2MG$ (1:6) explained by the following sequence of reactions.

$$LiAlH_4 + MgBr_2 \longrightarrow BrMgAlH_4 + LiBr \tag{30}$$

$$BrMgAlH_4 + 4(C_6H_5)_2Mg \longrightarrow BrMgAl(C_6H_5)_4 + 4(HMgC_6H_5) \tag{31}$$

When $LiAlH_4$ was allowed to react with C_6H_5MgBr in a 1:1 ratio the lower layer observed initially disappeared and the amount of solid increased relative to the amount observed when the reaction was carried out in 1:6 ratio. When the solid was filtered, elemental analysis showed a Mg:H ratio of 1.0:1.94. This analysis as well as infrared and X-ray

powder pattern analysis shows the solid to be MgH_2. The amount of magnesium in the solid accounts for 48.41 percent of the original magnesium. Elemental analysis of the filtrate showed a Br:Mg:Al ratio of 2.1:1.0:1.91. The infrared spectrum of the solution showed a broad band at 1750 cm^{-1}. These results are analogous to those observed in the reaction of $LiAlH_4$ with s-butylmagnesium bromide indicating that $HMgAlH_3C_6H_5$ disproportionates to MgH_2 and $Mg(AlH_3C_6H_5)_2$.

Reactions of Grignard Compounds with Excess $LiAlH_4$

Reactions of $LiAlH_4$ with Grignard reagents in ether at 1.0:1.0 stoichiometry of excess Grignard reagent have just been discussed. The importance of studying reactions in which $LiAlH_4$ is in excess is in the realization that $HMgAlH_3R$ compounds might be converted to $HMgAlH_4$ according to Eq. 32.

$$HMgAlH_3R + LiAlH_4 \text{ (excess)} \longrightarrow HMgAlH_4 + LiAlH_3R \qquad (32)$$

In this connection $LiAlH_4$ was allowed to react with $HMgAlH_3(n\text{-}C_4H_9)$ in 3:1 ratio. A trace amount of solid was obtained which gave a Mg:Al:H ratio of 0.0:1.0:2.8. After filtration the solvent was removed from the filtrate and the X-ray powder pattern of the resulting solid showed only lines corresponding to the starting material.

When $n\text{-}C_4H_9MgCl$ was added to $LiAlH_4$ in ether at a ratio of 1:4, a solid was obtained which after filtration was shown by elemental analysis and X-ray powder pattern to be LiCl. The solvent was then removed from the filtrate. The X-ray powder pattern of the resulting solid corresponded to a physical mixture of $LiAlH_4$ and $HMgAlH_3n\text{-}C_4H_9$. The results of

experiments indicate that $HMgAlH_3n\text{-}C_4H_9$ does not react with $LiAlH_4$ according to Eq. 32.

When sodium aluminum hydride was allowed to react with $n\text{-}C_4H_9MgBr$ in THF the products were somewhat different due to the insolubility of the NaBr by-product. At 1:1 ratio, a solid formed which had a Mg:Al ratio of 1.0:1.1. This solid accounts for about 10 percent of the original magnesium. The infrared spectrum of the solid corresponded to $Mg(AlH_4)_2 \cdot 4$ THF. The X-ray powder pattern of the solid shows lines corresponding to a physical mixture of NaBr and $Mg(AlH_4)_2 \cdot$ 4 THF. The elemental analysis of the solution gave a Br:Mg:Al ratio of 0.0:1.04:1.0. The infrared spectrum of the solution corresponds to $HMgAlH_3n\text{-}C_4H_9$. The $Mg(AlH_4)_2$ noted above could result from the reaction of $NaAlH_4$ with $MgBr_2$ present in the Schlenk equilibrium.

When $LiAlH_4$ is allowed to react with $n\text{-}C_4H_9MgBr$ in THF at a 1:1 mole ratio, no solid is formed. The infrared spectrum of the solution compounds to $HMgAlH_3(n\text{-}C_4H_9)$ as prepared in diethyl ether and redissolved in THF.

In the reaction of lithium aluminum hydride with isopropoxymagnesium bromide in a 1:1 mole ratio results similar to those obtained in the Grignard case were observed. Filtration of the reaction mixture yields a solution whose elemental analysis shows a Mg:Al:Br atio of 1.0:1.77:2.04. The infrared spectrum of the solid obtained by filtration corresponds to magnesium hydride and shows no bands characteristic of the Al-H stretching modes. These results indicate that the $(i\text{-}C_3H_7)MgAlH_4$ initially formed rearranges to $HMgAlH_3Oi\text{-}C_3H_7$ and then disproportionates to MgH_2 and $Mg(AlH_3Oi\text{-}C_3H_7)_2$.

$$C_2H_5MgBr + i\text{-}C_3H_7OH \longrightarrow i\text{-}C_3H_7OMgBr + C_2H_6 \quad (33)$$

$$i\text{-}C_3H_7OMgBr + LiAlH_4 \longrightarrow iPrOMgAlH_4 + LiBr \quad (34)$$

$$i\text{-}C_3H_7OMgAlH_4 \longrightarrow HMgAlH_3Oi\text{-}C_3H_7 \quad (35)$$

$$2(HMgAlH_3Oi\text{-}C_3H_7) \longrightarrow MgH_2 + Mg[AlH_3Oi\text{-}C_3H_7]_2 \quad (36)$$

Dibutylaminomagnesium aluminum hydride was prepared by the reaction of lithium aluminum hydride and di-n-butylaminomagnesium chloride in a 1:1 mole ratio. The elemental analysis of the solution obtained from filtration of the reaction mixture gave a Mg:Al:Cl ratio of 1.01:1.00:0.0. The infrared spectrum of the solution showed bands at 1830 (sharp), 870 cm^{-1} with a broad band at 740 cm^{-1}. The compound $(n\text{-}C_4H_9)_2NMgAlH_4$ is also soluble in benzene as the diethyl etherate.

$$(n\text{-}C_4H_9)_2NH + C_2H_5MgCl \longrightarrow (n\text{-}C_4H_9)_2NMgCl + C_2H_6 \quad (37)$$

$$LiAlH_4 + ClMgN(n\text{-}C_4H_9)_2 \longrightarrow LiCl + (n\text{-}C_4H_9)_2NMgAlH_4 \quad (38)$$

CHAPTER IV

CONCLUSION

The reaction of $LiAlH_4$ and $NaAlH_4$ with Grignard reagents has been show to lead to different products depending on the ratio of the reactants.

$$LiAlH_4 + 6\ n\text{-}C_4H_9MgBr \longrightarrow 2\ n\text{-}C_4H_9MgBr + 2\ MgH_2 + MgBr_2 + LiBr + BrMgAl(n\text{-}C_4H_9)_4$$

$$LiAlH_4 + 4\ n\text{-}C_4H_9MgBr \longrightarrow 2\ MgH_2 + MgBr_2 + LiBr + BrMgAl(n\text{-}C_4H_9)_4$$

$$LiAlH_4 + 3\ n\text{-}C_4H_9MgBr \longrightarrow MgH_2 + LiBr + 1/2\ MgBr_2 + BrMgAlH(n\text{-}C_4H_9)_3$$

$$LiAlH_4 + 2\ n\text{-}C_4H_9MgBr \longrightarrow BrMg_2AlH_4(n\text{-}C_4H_9)_2 + LiBr$$

$$LiAlH_4 + n\text{-}C_4H_9MgBr \longrightarrow HMgAlH_3n\text{-}C_4H_9 + LiBr$$

Various intermediates involved in the stepwise process, such as $BrMgAlR_4$ and $BrMg_2AlH_4R_2$, have been isolated and characterized. The stability of the $HMgAlH_3R$ compounds produced by the reaction of $LiAlH_4$ with RMgX in 1:1 ratio was found to be dependent on the nature of the alkyl group. When R=n-C_4H_9, C_2H_5 and C_6H_5 the $HMgAlH_3R$ compounds are stable. When R=CH_3 and s-C_4H_9, the compounds disproportionate to MgH_2 and $Mg(AlH_3R)_2$. The reaction in THF is very similar to that in diethyl ether except when the alkali metal by-product is insoluble in THF. In this case 10 percent of the magnesium and aluminum were isolated as a physical mixture of MgH_2 and $Mg(AlH_4)_2$ whereas the remainder of the product was found to be $HMgAlH_3R$ in solution.

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